med. Biochem Organothorax — 1510 (F)

Significance of phosphorus in formation of hydroxytetracycline. Z.M.Zaitseva and N.V.Orlova All Union Antibiotic Res.Inst.). Doklady Akad.Nauk SSSR, 124, 436-39(1959).

It was shown by growth of cultures of Act. rimosus that added P in the medium energizes the synthesis of nucleic acids, especially in the II phase of micellar growth. Acid-insol. polyphosphates are absent as a rule, but a difficultly hydrolyzable form of P accumulates to extent of 0.8% in the mycellium. Metabolism in general is stimulated by excess P in the medium, with increased yield of volatile acids, AcOH and pyruvic acids especially. However, excess P tends to reduce the yield of hydroxytetracycline by 5-6 fold. Addn. of excess P shifts the time of maximum P content in the mycellium to the 24 hrs. rather than normal 16 hrs. of duration of culture growth. Cf. Guberniev et al., Antibiotiki, No.3, 8 (1956).

G.M.Kosolapoff.

Bio

Some data on the mechanism of synthesis and utilization of polyphosphates in yeast

E.Bukhovich and A.N.Belozerskii. (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR 124, 1147-49 (1959).

Yeast (baker) is capable of incorporating P^{32} in the presence of dinitrophenol, the incorporation being in the orthophosphate and acid-soluble stable phosphorus compounds; entry into all other P derivs. is blocked. Removal of dinitrophenol results in rapid decline of the stable acid-sol. form and a rise in labile acid-sol. P. Adenosinetriphosphate activity also rises rapidly at this stage along with acid-insol. polyphosphates. Evidently the acid-sol. stable P passes into a labile form which is not a polyphosphate nor adenosinetriphosphate. Yeast were also grown on radioactive (P) or non-radioactive medium for 3 hrs., after which they were placed in P-free medium. This transfer results in rapid rise of ATP activity to the level of polyphosphates, possibly owing to a direct transfer of polyphosphate P to the adenylic system, which then controls the various synthetic routes. The orthophosphate activity rises rapidly after the transfer also and reaches the polyphosphate activity level in 15 min. The possible paths of polyphosphate metabolism are shown on a suggested chart.

G.M.Kosolapoff.

Precursors of purines of nucleic acids in higher plants.

Bio

G.I.Semenenko (A.M.Gorky State Univ., Kharkov). Doklady Akad. Nauk SSSR, 124, 1150-53 (1959).

Wheat and corn plants were grown in nutrient media and examined for purine content. Purine content rises in sprouts with the endosperm being intact. The best precursor for purines for sprouts with removed endosperm was glycine. Ribonucleic acid hydrolysate was also rather effective. C^{14}-labelled glycine (carboxyl label) shows active C^{14} incorporation into the purines. Wheat sprouts do not utilize nucleic acid purines for nucleic acid synthesis. The glycine incorporation involves adenine and guanine.

G.M.Kosolapoff.

Bio

Pigment synthesis in the roots.

B. A. Rubin and V. F. Germanova (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, 940-43 (1959).

It was shown that roots of bean, sunflower and nasturtium plants are capabl of synthesizing green and yellow plant pigments in approximately the same proportions as are found in the plant leaves, when the roots of the exptl. plants are kept under illumination. Thus, the bean plants form more chlorophyll than sunflower plants, while nasturtium forms the least amount. Caretenoids are formed to the greatest degree in sunflower roots or leaves. The plants which show a high order of synthetic activity for the green pigments also show a high order of activity of catalase and cytochromeoxidase in the roots.

G.M.Kosolapoff.

Bio

Effect of extraradical feeding on the alkaloid content and chlorophyll content in Datura inermis plants leaves.

S. E. Shpilenya (S.M.Kirov Milit.Med.Academy, Moscow). Doklady Akad. Nauk SSSR, 124, 944-46(1959).

Spraying of the above plants with solns. of $(NH_4)_2SO_4$ (1-2%) for extraradical feeding, resulted in improved growth of the plant and increased its alkaloid yield by some 50% at ripening period of the fruit.

G.M.Kosolapoff.

Bio

Effect of X-radiation on the content of nitrogenous substances in wheat. I. M. Vasil'ev, O. I. Parfenova and N. D. Pybalka. Doklady Akad. Nauk SSSR, 124, 928-29 (1959).

It was shown that 5000 r dose of X-radiation which totally suppressed the growth of 5-6 day wheat sprouts (winter wheat) does not suppress the formation of nucleotides and cyclic amino acids in the plants which form readily under conditions which are normally favorable for photosynthesis over several day period following the irradiation. The detection of the products was done spectrophotometrically only.

G.M.Kosolapoff.

Bio

Effect of chronic γ-irradiation on mouse blood. E. N. Kopylova. Doklady Akad. Nauk SSSR, 124, 930-32 (1959).

Mice subjected to daily dose of Co^{60} γ-radiation at 0.05-0.4 r daily show the symptoms of leuco- and lymphopenia after approximately a year. A daily dose of 0.1r produces hyperregeneration of white blood cells over that period. The small daily doses of radiation eventually cause a reaction which suppresses leucopoesis.

G.M.Kosolapoff.

Bio

Spectrophotometric study of the effect of pH and ionic strength on the stability of high polymeric ribonucleic acid in solution. L. P. Gavrilova, A.S.Spirin and A.N.Belozerskii (A. N. Bakh Biochem. Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 933-36 (1959).

It was shown that below pH 5 and above pH there exist zones of instability of highly polymeric ribopolynucleotide, possibly at the internucleotide P link to the ester groups. Between these limits, the substance is stable in any ionic strength of acetate, phosphate or glycine buffer soln. Cf. Reddi et al. Nature, 180, 374 (1957).

G.M.Kosolapoff.

Experimental formation of active variants of Aspergillus niger which form citric acid.

A. A. Imshenetskii, L. I. Solntseva and N. F. Kuranova. Doklady Akad. Nauk SSSR, 124, 925-27 (1959).

The commercial strain of A. niger subjected to ultraviolet light is prone to yield a mutant form, which forms colonies of different shape, which has a smaller dry weight of the mycelium, consumes more sugar and produces more citric acid than the original strain (yield may be as high as 74%). Gluconic and oxalic acid are formed in negligible amounts by the mutant.

G.M.Kosolapoff.

Structure of erysimoside -- a steroidal diglucoside from plants of Erysimum species.

V. A. Maslennikova, F. S. Khristulas and N. K. Abubakirov (Plant Substances Chem. Inst., Uzbek. Acad. Sci.). Doklady Akad. Nauk SSSR, 124, 822-25(1959) Paper chromatography with 1:1:1 MePh, BuOH and H_2O solvent system resulted in isolation from the Erysimum glucosides of a new substance named erysimoside, $C_{35}H_{52}O_{14}$,(I), amorphous solid, $[\ ]_D^{30}$ 16.5°, which gives the color tests typical of cardiac glucoside of the digitalis group; prolonged action of Ac_2O-pyridine gave an acetyl deriv., dec. 221-23°, $[\ ]_D^{25}$ 33.9°, which appears to be a pentaacetate, which saponifies to I with MeOH-$KHCO_3$. Hydrolysis with pancreatic juice of Helix plectotropis cleaves I to hexose and a monoglucoside; the hexose is D-glucose. The residual desglucoerysimoside forms needles, $C_{29}H_{42}O_9$ (from 60% MeOH), without a constant m.pt. Prolonged drying over P_2O_5 gave a product, m. 174-75°, $[\ ]_D^{20}$ 32.4°; vacuum drying gave a specimen, m. 152-55°. This gave color tests typical of a cardiac glucoside with a 5-membered lactone ring; the positive Keller-Kiliani test indicates that the aglucone is linked to a 2-desoxy sugar. In the above ternary solvent system this moves with strophantidine (Rf 0.85), but 1:1 $CHCl_3$-MePh separates these 2 substances. With Ac_2O-pyridine it gave a diacetyl deriv., m. 242-43°, $[\ ]_D^{20}$ 35.5°; no carbonyl group derivs. could be prepd. Mild acid hydrolysis of desglucoerysimoside gave an aglucone, prisms, m. 176-77°, $[\ ]_D^{19}$ 48.6° (monoacetyl deriv., m. 243°; phenylhydrazone, m. 241-42°), identified as strophantidine. The sugar component of the hydrolysis mixture was D-digitoxose. The results indicate that erysimoside is strophantidine (3)- -D-digitoxosido- -D-glucoside. It and olitoriside are diastereoisomeric substances. If the plant seeds are allowed to ferment for 3 days prior to isolation of the glucosides, the main isolable product of the glucoside group was desglucoerysimoside. The latter appears to be identical with helveticoside (Nagata et al. Helv. Chim. Acta, 40, 41 (1957)) and erysimotoxin (Maksyutina, Zhur.Obsh.Khim. 28, 1383 (1958).

G.M.Kosolapoff.

Bio

An organospecific liver antigen which is absent in hepatoma.
C.I.Abelev, Z.A.Avenirova, N.V.Engel'gardt, Z.L.Baidakova and G.I.Stepanchenok-Rudnik. Doklady Akad. Nauk SSSR, 124, 1328-30 (1959).
Examn. of cytoplasmic liver granules of mice with transplanted mouse hepatoma ~~Ex~~ (cf. Zil'ber et al. this j. 124, No.4 no pp (1959)) showed that in hepatoma the mouse liver lacks an atigen factor (named AO), which under normal conditions shows a very specific precipitation reaction and is found only in the liver. For isolation of this from normal mice an ultrasonic iiradiation in veronal-medianl buffer was used, since this antigen is more strongly bound to the cell walls than are other antigens. This reacted only with anti-MmP sera and did not react with antihepatomic sera. (MmP-mytochondrial and microsomal fraction of normal liver). AO did not migrate in sleotropheresis but this showed the presence in AO of a ballast lipoprotein. It is suggested that AO is principally a polysaccharide.

G.M.Kosolapoff.

Bio

Oxidative phosphorylation in the liver under the action of high oxygen pressure and introduction of I-131.
Z.G.Bronovitskaya (State Univ., Rostov-on-Don). Doklady Akad.Nauk SSSR, 124, 1331-34 (1959).
The phosphorylation coeff. was studied in rat livers under 6 atm. O_2 pressure ~~xxxhxcpxxxxxxxxxxxxxxxx~~. The expts. were run until violent convulsions of the animals produced a severe state of well-being. The results indicate that prolonged existence under high O pressure dissociates respiration from phosphorylation in the liver. High-energy compds. tend to accumulate in the liver and ATP content tends to drop owing to its consumption in the formation of these substances, as shown by lowered synthesis of ATP. Similar expts. with rabbits treated with I^{131} showed decreased assimilation of O and increased binding of inorg. P, with increased liver phosphorylation function.

G.M.Kosolapoff.

Bio

Nucleotide composition of nucleic acids of Bombyx mori.

N.M.Sisakyan and N.A.Gumilevskaya (A.N.Bakh Biochem. Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 1154-56 (1959).

The content of guanylic, adenylic, cytidilic and uridilic acids in pupae of Bombyx mori is tabulated. The results agree with the regularities observed by Chargaff (Biochem. Biophys. Acta, 17, 367 (1955)). Deoxyribonucleic acid content in this organism is rather low but the individual distribution again agrees with Chargaff's regularities (Experientia, 6, 201 (1950)).

G.M.Kosolapoff.

Bio

Selective inhibition of activity of oxidation-reduction enzymes in tumor cells after action of chain reaction inhibitors.

N.M.Emanuel, L.P.Lipchina, I.I.Pelevina and T.E.Lipatova. Doklady Akad. Nauk SSSR, 124, 1157-59 (1959).

The following expts. were run in vitro with tumor tissues from mice (various types of cancerous growths) and rabbits. Propyl gallate acts selectively on tumor cells at 0.75% concn. This action consists of repression of dehydrogenase activity and cytochromoxidase activity. The treated cells cannot be transplanted any longer and retain their activity as tumor cells.

G.M.Kosolapoff.

Bio

Peculiarities of electron structure of nucleic acids and their protein complexes.

L.A.Blyumenfel'd, A.E.Kalmanson and Shen Pei Gen. Doklady Akad. Nauk SSSR, 124, 1144-46 (1959).

Electron paramagnetic resonance spectra of nucleic acids and their protein complexes are shown and discussed. While yeast ribonucleic acid shows no wide band in the spectrum, its complex with serum and egg albumin show a very wide and intense band with 10^{21} unpaired electrons per g. The material remaining in soln. does not produce a spectrum. The no. of paramagnetic particles is constant in the temp.range down to 100°K, then drops to zero

G.M.Kosolapoff.

Reparative processes in the skin of young dogs after introduction of cortisone and the adrenal cortical hormone principle. Bio

A.I.Bukhonova. Doklady Akad. Nauk SSSR, 124, 477-80 (1959) (Voronezh State Med. Inst.).

Expts. with young pups from which a skin section had been removed while cortisone administration was being made daily at 20 mg daily (same for the adrenal hormone ext.) showed the course of the regenerative process, which is illustrated by numerous photographs. Both substances disrupt the formation of granulation tissues but accelerate its growth; the tissue tends to form superabundant amounts of dense connective tissue with high collagen content. The process of premature development and aging of the skin is observed.

G.M.Kosolapoff.

Bio

Effect of streptomycin on green coloration of sprouts.

B.A.Rubinand M.E.Ladygina (A.N.Bakh Biochem.Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 1163-66 (1959).

Streptomycin inhibits the cytochromoxidase activity in barley sprouts, the effect being blocked by Fe or Mn^{++}. These effects are directly correlatable with alterations in synthesis of chlorophyll by the plants. Thus, streptomycin by its effect of cytochromoxidase tends to retards chlorophyll formation and the green coloration of the sprouts. Fluorescence photography of sprouts of barley showed that the fluorescence spectra of plants with or without streptomycin are similar provided that light were excluded from the growing sprouts. The albino plants produced by streptomycin show spectra indicative of transition stages between protochlorophyll and chlorophyll. Evidently streptomycin tends to retard this transformation specifically.

G.M.Kosolapoff.

Action of intensity and spectral composition of radiation on metabolism and crop.

Bio

N.P.Voskresenskaya and G.S.Grishina (K.A.Timiryazev Plant Physiol.Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 469-72 (1959).

Expts. with kidney bean plants with environment being varied by the use of various levels of illumination with either red or blue lamps, showed that blue light aids the protein accumulation in the leaves, the effect being more pronounced at light light intensities. The cytochrome system activity is higher in leaves grown in blue light, as an adaptation phenomenon evidently. Protein synthesis is aided by the blue light, this effect leading to a rise in seed crop and that of accumulated nitrogenous products.

G.M.Kosolapoff.

Bio

Volatile emanations of flowers and alteration of sex symptoms in corn.

G.V.Porutskii and S.V.Cherednichenko. Doklady Akad. Nauk SSSR, 124, 473-76 (1959).

The connection between activity of volatile products and sex symptoms changes in corn was examined by introduction of radioactive thiamine into the plants during flowering, with subsequent tracing of later generations. The results indicate that radioactive thiamine aids the predominant development of the stamen- carrying flowers with a sharp reduction of the activity of the volatile excretions of the individual flowers; the activity of the volatiles from pistillate flowers rises at the same time. Typical plants are shown. Irregular ears of corn are commonly produced.

G.M.Kosolapoff.

Bio

Some data on invertase activity in isolated lucerne roots. M.S.Bardinskaya, A.M.Smirnov and V.I.Safonov (K.A.Timiryazev Plant Physiol. Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 462-65 (1959).
The isolated lucerne roots from plants grown for prolonged periods in sterile medium possess noticeable amounts of invertase which can cleave sucrose and which can accomplish the transfer reactions forming oligosaccharide containing fructose and -methylfructoside. The activity of the enzyme drops by 7 days of culturing and at this time the nutrient medium begins to show a rise in alkalinity. The enzyme concn. is highest in the growth zones of the roots.

G.M.Kosolapoff.

Bio

Effect of environmental conditions on respiration intensity in cuttings treated with heteroauxin.
V.F.Verzilov and L.V.Runkova. Doklady Akad. Nauk SSSR, 124, 466-8 (1959).
Expts. with bean plant cuttings which were rooted at 12-14° or 18-20° under various light intensities and with or without treatment with heteroauxin, showed that the treatment lowers the respiration level in cuttings kept at 18-20° with strong illumination in the leaf tissue but raises it in the lower parts of the stem, this being true during root formation. The heteroauxin action was lower at lower temp. and lower light intensity. Thus the heteroauxin effect is aided by higher temp. and more intense light.

G.M.Kosolapoff.

Bio

Influence of penicillamine on decarboxylation of amino acids by microbial preparations.

S.R.Mardashev and L.A.Semina (I.M.Sechenov 1st Moscow Med. Inst.). Doklady Akad.Nauk SSSR, 124, 456-58 (1959).

Penicillamine added at 10^{-2}-10^{-4}M concns. to cultures of Bac. cadaveris blocks the decarboxylation of lysine, the effect being rather weak at 10^{-4}M, but pronounced at 10^{-2}M. E. coli decarboxylase is similarly repressed in its decarboxylation of arginine substrate by the presence of penicillamine. Other microbial specimens gave results that were not clear-cut. Al, Fe, Cu or Zn ions do not remove this blocking effect of penicillamine.

Cf.Snell et al.JACS 76, 4745 (1954). G.M.Kosolapoff.

Bio

Participation of alanine in biosynthetic processes in plants.

E.A.Shilov and A.A.Yasnikov (Inst. Org. Chem., Kiev). Doklady Akad. Nauk SSSR, 124, 459-61 (1959).

The participation of alanine in biosynthetic processes in plants (kok-sagyz) evidently depends on the ability of alanine to form AcOH and MeC(:NH)H as precursors for other products. C^{14}-labelled alanine specimens were traced through the kok-sagyz plants showing: very rapid C^{14} uptake from alanine into the rubber, cellulosic matter, fatty acids but very little in glycerol. The incorporation of C^{14} from alanine in carotene is relatively slow. The possible reaction courses are discussed.

G.M.Kosolapoff.

Bio

The paths of influence of ionizing radiation on the content of free nucleotides and nucleosides in bone marrow cells.

V.Ya.Brodskii, E.Ya.Graevskii and I.A.Suetina (A.N.Severtsov Animal Morphol. Inst., Moscow). Doklady Akad.Nauk SSSR, 124, 440-43 (1959).

X-irradiation (700 r) of white mice at 94 r/min. results in decline of the nucleotide content in the animal tissue, whether directly irradiated or screened from direct radiation. The results were shown graphically.

Cf. Brodskii et al. Biofizika, 3, 92(1958). G.M.Kosolapoff.

Bio

Electrophoretic properties of some protein components of blood clotting.

B.A.Kudryashov, G.V.Andreenko and G.V.Kukushkina. (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, 452-55 (1959)

Electrophoretic sepn. of X and VII blood clotting factors isolated from sera of horse and rat blood was studied and the electrophorograms are shown. Factor VII is inhomogeneous are shows 2 bands indicative of - and γ-globulins with the former predominant. Factor X is practically completely composed of γ-globulins. Almost 100% of factor X protein and 81% of factor VII protein is collected in the electrophoretic peaks. The results indicate that factors VII and X and thrombotropin all have different electrophoretic mobilities. Thrombotropin is homogeneous and is composed of -globulin. It is possible that factor VII is blood thrombokinase and thrombotropin, these being the immobile and the mobile fractions, respectively, in electrophoresis.

G.M.Kosolapoff.

Nitrogen bond equivalence in tetramethylammonium bromide.

A. T. Babayan, M. G. Indzhikyan and M. B. Neiman. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 174.

$C^{14}H_3Me_3NBr$ was prepd. from $(C^{14}H_3)_2SO_4$ by treatment with KBr and Me_3N, the last reaction being run at -80°. The resulting product was treated with K in NH_3 over 1 week; the resulting CH_4 was analyzed for C^{14} content. The resulting Me_3N was converted to HCl salt and burned for C^{14} analysis. It was shown that the evolved CH_4 carried 23% of C^{14}, while Me_3N contained 78%. Thus the work confirms the equivalent nature of N bonds in Me_4NBr.

G.M.Kosolapoff.

Organic

A synthesis of 1,1-dicyclopentylethane and 1,2-dicyclopentylpropane based on cyclopentadiene.

V. I. Stanko and A. F. Plate (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 115-120.

To 40 g. Mg under Et_2O there was added a mixture of 75 g. EtOAc and 174 g. -2-cyclopentenyl chloride in Et_2O; after refluxing for 3 hrs. on the following day, the mixture was treated with dil. H_2SO_4 yielding 58 g. bis-(2-cyclopentenyl) (I), b_{14} 65.6°, n_D^{20} 1.4941, d_{20} 0.9072, and 22 g. bis-(2-cyclopentanyl)-methylcarbinol, b_6 113-22°; repeated fractionation finally gave but 6 g. of the pure carbinol, $b_{3-3.5}$ 104.5-105.9°, 1.5121, 1.0014. Hydrogenation of I over Raney Ni in the cold in EtOH gave dicyclopentyl, b_{750} 189.5-89.7°, 1.4650, -. Part of this was purified by passage over SiO_2, the other was frozen out; the pure product had f.p. -35.5° to -35.6°, n_D^{20} 1.4643, d_{20} 0.8656, b_{750} 189.5-189.7°. Reaction of AcCl with cyclopentene gave methyl cyclopentyl ketone, b_{749} 157.5-58°, 1.4432, 0.9161. This condensed with cyclopentadiene in the presence of EtONa-EtOH in 2 hrs. gave a crude product which was directly hydrogenated over Raney Ni at 90° to 9% 1,1-dicyclopentylethane, b_9 98-100°, 1.4740, 0.8780. Alternatively, hydrogenation of methyl cyclopentyl ketone over Raney Ni at 90 atm. and 150° gave 1-cyclopentylethanol, b_{10} 160-62°, 1.4570, 0.9189, which with HBr-H_2SO_4 at 0°, room temp. and finally at steam bath temp 2 hrs. gave 1-bromo-1-cyclopentylethane, 39%, $b_{7.5}$ 49-50°, 1.4878, 1.2628, which was converted to the Grignard reagent and treated with 2-cyclopentenyl chloride, yielding a small amount of 1(2-cyclopentenyl)-1-cyclopentylethane, b_8 96.5-97°, 1.4855, 0.8988, which hydrogenated over Raney Ni to 1,1-dicyclopentylethane, 21%, b_{14} 102-102.5°, 1.47387, 0.8792. Reaction of cyclopentylmagnesium bromide with allyl chloride gave 57% allylcyclopentane, b_{749} 125.8-26.2°, 1.4408,-, which with HBr at -30° gave 61% 2-bromo-1-cyclopentylpropane, b_{30} 99.5°, 1.4818, 1.2126, which converted to the Grignard reagent and treated with 2-cyclopentyl chloride with ice cooling gave in 2 hrs. 55.5% 1-(2-cyclopentenyl)-2-cyclopentylpropane, b_{18} 122.5°, 1.4796, 0.8832, which hydrogenated over Raney Ni

to 50% 1,2-dicyclopentylpropane, b_{14} 117.5-18°, 1.47041, 0.8695, purified by passage over AlO_2 and careful fractionation.

G.M.Kosolapoff.

Organic

Action of Raney nickel on ketones and acetals of the thiophene series. Ya. L. Gol'dfarb and P. A. Konstantinov (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 121-29. Cf. this j. 1956, 992.

Stirring 11 g. t-butyl 2-thienyl ketone and 80 g. Raney Ni in EtOH-C_6H_6 18 hrs. gave 41% Me_3CCOBu, b. 164-66°, n_D^{20} 1.4163, d_{20} 0.8211, whose 2,4-dinitrophenylhydrazone, m. 117.5-18°. Condensation of 3.36 g. 2,5-dimethylthiophene with 5 g. 2,5-dimethyl-3-thiophenecarboxylic chloride in C_6H_6 in the presence of 7.5 g. $SnCl_4$ gave 91% 2,2',5,5'-tetramethyl-3,3'-dithienyl ketone, m. 63-64° (from aq. EtOH). Reaction of $SOCl_2$ with 2,5-bis-tert-butyl-3-thiophenecarboxylic acid gave the acyl chloride, 90%, b_7 129-30° which with 2,5-bis-tetrt-butylthiophene in the presence of $SnCl_4$ at 0°, finally at room temp., gave 80% 2,2',5,5'-tetra-tert-butyl-3,3'-diethienyl ketone, m. 213-18° (crude), m. 221-22° (from EtOH). Refluxing this with Raney Ni in EtOH-C_6H_6 gave no evidence of reaction even in 18 hrs. Stirring 25.4 g. $POCl_3$, 21.2 g PhNMeCHO 0.5 hr. at room temp., addn. of 24 g. 2,2-di-(2-thienyl)-butane and keeping the mass overnight gave after an aq. treatment 64% 2-(2-thienyl)-2-(5-fornyl-2-thienyl)butane, b_3 160-62°, 1.6120, 1.2016; oxime, m. 103-104°. Refluxing 10.8 g. 2-thiophencarboxaldehyde, 10 g. $(CH_2OH)_2$ and 0.2 g. p-Me-$C_6H_4SO_3H$ in C_6H_6 with continuous removal of H_2O over 16 hrs. gave 81% 2-thiophenecarboxaldehyde ethylene acetal, b_{24} 121-22°, b_{15} 110-11°, 1.5435, 1.2395. Similarly was prepd. 5-(2-thenyl)-2-thiophenecarboxaldehyde ethylene acetal, b_5 178-81°, b_5 179-80°, 1.5992, 1.2789; 5-butyl-2-thiophenecarboxald-

ehyde ethylene acetal, 77%, b_8 132-33°, 1.5190, 1.0987; 2-(2-~~mix~~thienyl)-2-(5-formyl-2-thineyl)butane ethylene acetal, &&-, b_4 187-88.5°, 1.5827, 1.2094. Treatment of 2-thiophenecarboxaldehyde ethylene acetal with Raney Ni in Et_2O 12 hrs. gave 42% valeraldehyde ethylene acetal, b_{34} 53-55°, 1.4211, 0.9269. Similarly 5-butyl-2-thiophenecarboxaldehyde ethylene acetal gave 58% pelargonaldehyde ethylene acetal, b_{17} 113.5-15.5°, 1.4400, 0.9002, which on hydrolysis gave 2,4-dinitrophenylhydrazone, m. 106-107°, which agreed with an authentic specimen from pelargonaldehyde (cf. Strain, ~~JACS~~ 57, 758(1935)) 5-(2-thienyl)-2-thiophenecarboxaldehyde gave 33% capraldehyde ethylene acetal, b_{15} 121-24°, 1.4390, 0.8923. 2-(2-thienyl)-2-(5-formyl-2-thienyl)-butane ethylene acetal gave 43% δ-methyl-δ-ethylcapraldehyde ethylene acetal, b_7 128-32°, 1.4530, 0.9024; the hydrolyzed specimen gave the 2,4-dinitrophenylhydrazone of the free aldehyde, m. 64.5-65.5°.

G.M.Kosolapoff,

Organic

Micro determination of the carbonyl group by oximation method.
V. A. Klimova and K. S. Zabrodina (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 175-76.

The following micro detn. of CO groups is described; it is accurate within 0.2%. To 5 ml. of reagent soln. (0.7 g. $HONH_2.HCl$, 10 ml. H_2O, 0.5 g. $(HOCH_2CH_2)_3N$ and 96% EtOH to give 100 ml.) was added 5-10 mg. of sample and the whole is kept 0.5 hr. at room temp. along with a blank. Then 2 ml. satd. NaCl soln. was added and 3 drops of indicator soln. (0.1 g. bromophenol blue in 100 ml. 20% EtOH) and the soln. is titrated with 0.02N HCl to bluish-green color. To get a better color match with the blank, the test sample soln. is dild. with H_2O whose volume is about equal to the vol. of standard HCl indicating the difference between the 2 titrations and the content of CO is calcd. with due allowance for this diln. A variety of carbonyl compounds were successfully analyzed in this manner (table shown).

G.M.Kosolapoff.

Benzophenone and $Hg(OAc)_2$ in C_6H_6 at 70° gave 92% oily diphenylacetoxy-acetoxy ~~chlorx~~mercurimethane, which gradually decomposed to Ph_2CO and Hg; with alc. $CaCl_2$ it gave diphenylacetoxychloromercurimethane, a solid which is rapidly decomposed on standing or on treatment with alkalies; with alc. KOH it gave Ph_2CO and Hg; on heating to 100° it gave Hg and Ph_2CO. Similar reaction of $Hg(OAc)_2$ in C_6H_6 with $o\text{-}O_2NC_6H_4CHO$ hydrazone gave 80% oily, unstable o-nitrophenylacetoxyacetoxymercurimethane, which with alc. $CaCl_2$ gave a yellowish solid o-nitrophenylacetoxychloromercurimethane, dec. above 135° (from aq. EtOH); with alc. KOH it gave Hg and the original aldehyde.

G.M.Kosolapoff.

Organic

An error.

E. Nikitina. Zhur. Obshchei Khim. 29, 696 (1959). NO RQ

The paper in this j. 26, 621(1956) contains an error. At 109° the acid described therein should be a hydrate $H_7[P(W_2O_7)_6].4H_2O$, not $.H_2O$.

G.M. Kosolapoff.

Organophosphorus (8)

Extraction of ruthenium nitrosonitrate by esters. ← Butylphosphorous compounds.

A. V. Nikolaev and N. M. Spitsyn (Inorg.Chem.Inst., Siberian Section, Acad. Sci). Doklady Akad. Nauk S.S.S.R. 127, 117-9(1959).

Extn. of Ru nitrosonitrate from N HNO_3 was performed with $(BuO)_3PO$, $BuP(O)(OBu)_2$ and $Bu_2P(O)OBu$. The efficiency of extn. increased considerably in the above order of extractants, the last substance being able to effect a 88% extn. At very low concns. of the extractants in the org. phase, the results were relatively close to each other. It is suggested that Me_3C groups should give the highest extn. efficiency. Cf. Burger, J. Phys.Chem. 5, 62, 520 (1958).

G.M.Kosolapoff.

Organophosphorus

Extraction of nitric acid by derivatives of butylphosphonic acids. A. V. Nikolaev, S. M. Shubina and N. M. Sinitsyn (N. S. Kurnakov Inst. Gen. Inorg. Chem.). Doklady Akad. Nauk S.S.S.R. 127, 578-80 (1959). cf. Berger, J. Phys. Chem. 62, 590 (1958).

It was shown that HNO_3 is extd. from aq. solns. progressively better by hydrocarbon solns. of $(BuO)_3PO$, $BuP(O)(OBu)_2$, $Bu_2P(O)OBu$ and Bu_3PO. The results are shown graphically and tabularly at different concns. of the extractants in the hydrocarbon medium. Only $BuP(O)(OBu)_2$ used at concn. above 50% in the hydrocarbon solvent shows a declining efficiency of extn. of HNO_3; this is not shown by the other substances and no explanation for this phenomenon is given. The extns were run from N HNO_3 in the presence of 30 g./l. uranyl nitrate. Extn. with Bu_3PO in hydrocarbon system gave a 2nd organic layer evidently of a complex between Bu_3PO and HNO_3; this was not observed if the org. fluid was CCl_4. At concn. range of 0-50% of the extractant in the org. phase, there is a decline of extn. of HNO_3 in the presence of UO_2 ion in passing from $(BuO)_3PO$ to Bu_3PO, this being caused by greater effectiveness of the C-P linked substances to extract U and to undergo a displacement of the sorbed HNO_3 by the uranyl groups.

G.M.Kosolapoff.

Niobium analog of phosphonitrilic chloride.

I. V. Tananaev, G. B. Seifer and E. A. Ioneva (N.S.Kurnakov Inst. Gen. Inorg Chem.). Doklady Akad. Nauk S.S.S.R. 127, 584-5 (1959).

Heating $NbCl_5$ with large excess of NH_4Cl finally to 250-60°(removal of unreacted mate ials in vacuo at 325°) gave a yellow-brown solid which is slowly hydrolysed by H_2O. The substance is close to $NbNCl_2$; d_{20} 2.05. The thermogram of decompn. under A gave an endothermic effect at 420-60°, when NbN and Cl_2 are formed. The substance is anisotropic and has very high n.

G.M.Kosolapoff.

Synthesis of some triethylsiloxyalkoxytitanium compounds. Organic

K. A. Andrianov and V. V. Astakhin. Doklady Akad. Nauk S.S.S.R. 127, 1014-5 (1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1958,644.

Slow distn. of BuOH through a fractionating column from 105.6 g. Et_3SiOH, 136 g. $Ti(OBu)_4$ and 0.02 g. Na gave 34% $(BuO)_2Ti(OSiEt_3)_2$, b_4 182°, d_{20} 0.9517, n_D^{20} 1.4758. Similarly, 68 g. $Ti(OBu)_4$ and 79.2 g. Et_3SiOH with 0.015 g. Na gave 90% BuOH and 46% $(Et_3SiO)_3TiOBu$, b_3 174-7°, 0.9378, 1.4687. Similarly 113.6 g. $Ti(OPr)_4$ and 105.6 g. Et_3SiOH with 0.02 g. Na gave 95% PrOH and 21% $(PrO)_2Ti(OSiEt_3)_2$, $b_{1.5}$ 144-6°, 0.9680, 1.4800. Cf. Brown et al. JACS 79, 4616(1957).

G.M.Kosolapeff.

Organic

Esters of thieboronic acids and some of their transformations.

B. M. Mikhailov, T. K. Kozminskaya, N. S. Fedotov and V. A. Dorokhov (N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R., 127, 1023-6 (1959). cf. Izvest.Akad.Nauk SSSR, Otd.Khim.Nauk 1959, 172.

Refluxing 20.5 g. $PrBBr_2$ and 23 g. BuSH 13 hrs. gave 90% $PrB(SBu)_2$, b_{13} 149-50°, d_{20} 0.9106, n_D^{20} 1.4956. Similarly was prepd. 88.5% $BuB(SBu)_2$, b_7 148-50°, 0.9045, 1.4936; 80% iso-$AmB(OBu)_2$, b_6 153.5-4°, 0.8988, 1.4871; 53% $PhB(SBu)_2$, $b_{1.5}$ 137.5-8.5°, 0.9865, 1.5464; 69% Ph_2BSBu, b_7 178-80°, 1.001, 1.5871; 80% $(1\text{-}C_{10}H_7)_2BSBu$, b_2 245-7°. Heating 11.6 g. iso-$AmB(SBu)_2$ with 2.68 g. $(CH_2NH_2)_2$ 2 hrs. at 150° gave 90% BuSH and 85.5% 2-isoamyl-2-bora-1,3-diazolidine, b_{12} 80-1°, 0.9165, 1.4872; this formed in 77% yield from 14 g. iso-$AmBCl_2$ and 11 g. $(CH_2NH_2)_2$ in Et_2O. $PrB(SBu)_2$ similarly gave 83.5% 2-propyl-2-bora-1,3-diazolidine, b_{25} 67-8°, 0.9406, 1.4941. Passage of NH_3 over 40 min. into 10.3 g. iso-$AmB(SBu)_2$ gave 84.5% BuSH and 87.7% B-triisoamylborazol, $b_{0.1}$ 114-5.5°. Similarly $PhB(SBu)_2$ gave 95% B-triphenylborazol, m. 178-80°. Heating 9.9 g. $PhB(SBu)_2$ and 6.1 g. Et_2NH 5 hrs. at 95° gave 80% $PhB(NEt_2)_2$, $b_{2.5}$ 115.5-6.5°, 0.9406, 1.5183. Ph_2BSBu and iso-$BuNH_2$ in 1 hr. gave 80.7% $Ph_2BNHCH_2CHMe_2$, b_8 161-3°,-,1.560. Ph_2BSBu and NH_3

gave in 1 hr. 85.4% Ph_2BNH_2, m. 141-2°. Similarly was prepd. 70% $(1\text{-}C_{10}H_7)_2BNH_2$, m. 113-4°.

G.M.Kosolapoff.

Organic

Synthesis and transformations of oxygen-containing organosilicon compounds. 8. Synthesis and properties of low molecular weight ethers of methyl-α-naphthylsilanediol.

M. F. Shostakovskii and Kh. I. Kondrat'ev (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1041-8. cf.1956, 970.

Addn. of 31 g. α-$C_{10}H_7SiMeCl_2$ ($b_{1.5}$ 123-5°, d_{20} 1.2357, n_D^{20} 1.6026) over 1.5 hrs. to 125 ml. H_2O, 0.14 mole MgO and 130 ml. Et_2O at 0° gave on evapn. of the org. layer 88.4% crude α-$C_{10}H_7SiMe(OH)_2$ (I), contg. $H(OSiMeC_{10}H_7)_nOH$. This distd. with BuOH gave 20.3% α-$C_{10}H_7SiMe(OBu)_2$, b_{14-15} 196-204°, $b_{2-2.5}$ 168-70°, 0.9987, 1.5270, 37.7% $(\alpha\text{-}C_{10}H_7SiMeOBu)_2O$, b_{14-15} 297-312°, b_2 238-44°, 1.0730, 1.5995, and 26.7% $BuO(C_{10}H_7SiMeO)_3Bu$, b_{14-15} 348-52°, $b_{1.5-2}$ 297-304°, 1.1183,-. Decreasing the amt. of BuOH tends to reduce the amts. of the less complex products, the main product being $BuO(C_{10}H_7SiMeO)_4H$, b_{14-15} 367-84°, $b_{1.5-2}$ 334-44°, 1.1448,-. Reaction of α-$C_{10}H_7SiMeCl_2$ (228 g.) with BuONa (from 42 g. Na) in MePh at 11-19° gave 86% α-$C_{10}H_7SiMe(OBu)_2$, $b_{2-2.5}$ 166-72°, 0.9987, 1.5268, and 5-6% II. Addn. of 49 g. BuOH of 40 g. α-$C_{10}H_7SiMeCl_2$ over 3 hrs. at room temp. in vacuo followed by 2 hrs. at 35-76° at 32-40 mm. gave 47 g. Cl-contg. product which treated with BuONa gave some $C_{10}H_8$, 60% α-$C_{10}H_7SiMe(OBu)_2$ (III) and 11% II. Heating III with H_2O gave no hydrolysis in 1 hr. at 120-30°; the result was the same in H_2O-BuOH mixt.

G.M.Kosolapoff.

Organic

Extraction isolation of pentavalent neptunium.

A. ..Alimarin, ..u. ..olotov and ..I. ..ol'shin (V.I. Vernadskii Geochem. and Anal. Chem. Inst.), Doklady Akad. Nauk SSSR, 124, 328-30 (1959).

Np^V may be extd. by solns. of 1-nitroso-2-naphthol in BuOH or iso-AmOH at pH 8-10. The work was explored with tracer quantities, then checked on gravimetric amounts. The necessary Np^V was formed by reduction of Np^{VI} with hydr... ...acid and was adjusted to the desired pH with NH_4OH-NO_3. The naphthol extractant was used as 1% soln. in the desired alc. Below pH 6 no extn. takes place; the best extn. occurs at pH 8-10 with 90-..% extn. with BuOH in 1 extn. with equal vols. of the 2 layers; iso-AmOH gave 80-.. extn., AcOEt, $CHCl_3$ and ... are less effective. At pH above 8-10 ... of the extractant occurs with most solvents, but with ... this occurs only above pH 11.4. Reduction of extractant concn. ... useful ... for extn. and gives a cleaner ... Interferences are cited as: F^-, CO_3^{--}, PO_4^{---}, $..O^-$, citrate. ... severe interference or hindrance is caused by ethylenediaminetetraacetic acid; small amounts of fluorides or carbonates are not harmful. Nitrates, chlorides or sulfates do not interfere. The extn. depends on interaction of NpO_2^- ion with the naphthol extractant. The procedure is useful for sepn. of Np from U and Pu. Uranyl ion ... extd. at pH 3.5-4 (or above), Np^V is not extd. Pu^{IV} can be extd. at pH 1-1.5. Since it is possible to obtain solns. contg. U^{VI}, Np^V and Pu^{IV}, (as for example with $NaNO_3$), the possibility for sepn. of these is evident.

G. M. Kosolapoff.

Organic

Effect of ... on ... of oxidation of carbon chain polymers.

V. ..Yur'ev, ...ovchinnikov and ... Medvedev. Doklady Akad. Nauk SSSR, 124, 335-37 (1959).

Direct action of O_3 at 100-250° was examined with specimens ...rene, polymethylene, polymeric hydrocarbons with side-chain...

decompn. of diazomethane, diazobutane, diazoethane., and poly-p-isopropylstyrene. The kinetic curves are reproduced. In general, side-chains are sites for active oxidation and their presence increases O_2 uptake very considerably. The aliphatically branched polymers show evidence of some cross linking during the oxidation, this being evidently caused by O-bridging during the radical reaction. Polystyrene did not show this behavior in the group of polymers studied.

G.M.Kosolapoff.

Organic

Synthesis of ferrocene derivatives with N,N-dimethylaminomethylferrocene methiodide.

A.N.Nesmeyanov, E.G.Perevalova, L.S.Shilovtseva and Yu.A.Ustynyuk (M.V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, 331-34 (1959) (I)

Heating 1.1 g. N,N-dimethylaminomethylferrocene methiodide and 1.5 g. $Na_2SO_3 \cdot 7H_2O$ in 60 ml. H_2O 7 hrs. at 80°, treatment with $Ba(OH)_2$, removal of excess Ba with CO_2, concn. of the filtrate, gave 77% Na ferrocenylmethanesulfonate monohydrate, crystals (from H_2O or EtOH), does not m. 330°. I and aq. KCN in 5 hrs. of reflux gave 46% ferrocenylmethyl thiocyanate, m. 59-61° (from petr. ether). I with PhOH and NaOH in 5 hrs. at 80-90° gave after usual ac. treatment 30% phenyl ferrocenylcarbinol ether, m. 129-30° (from petr. ether). Similarly was prepd. 2-naphthyl ferrocenylcarbinyl ether, dec. 121-23° (from petr. ether). To 0.5 g. p-$HOC_6H_4N_2Cl$ in 5% NaOH was added aq. soln. of 1 g. I and after 20 hrs. at 100° there formed a ppt. of 50% p-ferrocenylmethoxyazobenzene, dec. 155.5-57.5° (from C_6H_6). To 20.8 g. Et_2NH in 50 ml. AcOH was added 6.4 g. paraformaldehyde and 18.6 g. ferrocene; after 10 hrs. at 80-100°, this was dild. with H_2O, filtered from unreacted ferrocene, the aq. soln. made alkaline and extd. with Et_2O, yielding some 2g. steamdistillable N,N-diethylaminomethylferrocene, isolated as methiodide, dec. 159-62° (from EtOH). Heating 30 g. methyl-

ferrocene, 15.3 g. $CH_2(NMe_2)_2$, 4.5 g. paraformaldehyde, 30 g. H_3PO_4 (D. 1.73) and 200 ml. AcOH 7 hrs. at 95° gave after distn. of the products in vacuo over Zn dust 80% N,N-dimethylaminomethyl-methylferrocene, b_1 115-18°, b_5 138-40°, n_D^{20} 1.5612, d_{20} 1.2150 (infra red spectrum is indicated), and 19% bis-(N,N-dimethylaminomethyl)-methylferrocene, b_1 130-31.5°, 1.5622, 1.1260 (infrared spectrum indicated). The former yields the methiodide (II), dec. 185° (from MeOH-Et_2O). If the H_3PO_4 is omitted, the yield of the mono-deriv. is 60% (74% if isolated as the methiodide). If the reaction is run at 110-15° 10 hrs. the yield of the mono-deriv. is 42% and that of disubstituted product is 32%. Reduction of II with Na-Hg gave 75% dimethylferrocene, b_4 77°, b_{13} 119°, 1.6007, 1.2458, n_D^{25} 1.5922 (infrared spectrum indicated). The spectrum indicates that the product is homoannular and that the Me groups are probably in 1,3-positions.

Fluoroorganosilicon compounds. Addition reaction of alkylchlorosilicon hydrides to 1,1,2,2-tetrafluoroethyl allyl ether.

A. D. Petrov, V. A. Ponomarenko, G. V. Odabashyan amd S. I. Krokhmalev (N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk SSSR, 124, 838-41 (1959). Cf. 121, No.2 (no pp) (1958).

Heating 40.6 g. Cl_3SiH with 47.5 g. $CH_2:CHCH_2OCF_2CF_2H$ at 161° with 0.3 g. 1% Pt-C 3 hrs. in autoclave gave 58% $Cl_3SiCH_2CH_2CH_2OCF_2CF_2H$, b_{751} 186°, d_{20} 1.4335, n_D^{20} 1.3994. Similarly were obtained: $Cl_2SiMeCH_2CH_2CH_2OCF_2CF_2H$, 35%, b_{750} 190.1°, 1.3140, 1.3960; $Cl_2SiEtCH_2CH_2CH_2OCF_2CF_2H$, 63%, b_{749} 207.2°, 1.2837, 1.4033; 40% $Cl_2SiPrCH_2CH_2CH_2OCF_2CF_2H$, b_{11} 101°, 1.2484, 1.4062; and 46% $MeEtClSiCH_2CH_2CH_2OCF_2CF_2H$, b_{749} 199°, 1.1681, 1.3956. Reaction of $MeEt_2SiH$ and the above ether occurred exothermically in iso-PrOH when H_2PtCl_6 soln. was added to the components and gave in 30 min. 28% $MeEt_2Si-CH_2CH_2CH_2OCF_2CF_2H$, b_{749} 196.5°, 1.0422, 1.3930. The above halogen derivs. gave with MeMgBr: 58.9% $Me_3SiCH_2CH_2CH_2OCF_2CF_2H$, b_{746} 156°, 1.0453, 1.3732; 67.5% $Me_2EtSiCH_2CH_2CH_2OCF_2CF_2H$, b_{739} 176°, 1.0402, 1.3830; 57.3% $Me_2PrSi-CH_2CH_2CH_2OCF_2CF_2H$, b_{751} 193°, 1.0267, 1.2886. $Me_3SiCH_2CH_2CH_2OH$ was treated with Na and the product in autoclave with $CF_2:CF_2$ at 10 atm. gave 48.7% $Me_3SiCH_2CH_2CH_2OCF_2CF_2H$, identical with the above. $Me_3SiCH_2CH_2OH$ similarly gave 21.6% $Me_3SiCH_2CH_2OCF_2CF_2H$, b_{746} 137°, 1.0427, 1.3732.

 solapoff.

Organic

Reactions of hexafluoro-1,3-butadiene with alcohols and amines. I.L.Knunyants, B.L.Dyatkin and L.S.German (Inst. Hetero-Org. Compounds, Moscow). Doklady Akad. Nauk SSSR, 124, 1065-68 (1959).

Keeping 21 g. hexafluoro-1,3-butadiene (I) in 200 ml. abs. EtOH contg. 4.8 g. Na with ice cooling 1 day gave, after quenching in dil. HCl and washing, an oil which evolved some HF during distn. and yielded 18.9 g. product with b_{17} 45-83°. Treated with silica gel, this evolved more HF with heat evolution. On the following day the product was taken up in Et_2O, washed with H_2O and distd. yielding 41.8% 1,4-diethoxyperfluoro-1,3-butadiene, b_{17} 83-85°, n_D^{20} 1.3871, d_{20} 1.1883 (Infrared spectrum shows a band at 1740 cm^{-1}). This (9 g.) in 20 ml. CH_2Cl_2 was treated over 2 hrs. with 2.5 ml. concd. H_2SO_4 and after shaking several hrs. and standing overnight, the mixture yielded after an aq. treatment 83.6% di-Et fluoroethylenedicarboxylate, $EtO_2CCF{:}CH{-}CO_2Et$, $b_{1.5}$ 74°, 1.4330, 1.1456. I (16.2 g.), 6 ml. dry MeOH and 0.8 ml. Et_3N were heated 4 hrs. at 90-100° in steel ampul; after treatment with dil. HCl there was obtained 50% 1-methoxyhydroperfluoro-2-butene, $MeOCF_2CF{:}CFCF_2H$, b_{143} 30-31°, 1.3030, 1.3696 (infrared spectrum has a band at 1700 and 1730 cm^{-1}). Similarly EtOH gave 53.5% EtO analog, b_{144} 48.5°, 1.3270, 1.3090 (infrared spectrum has bands at 1730 and 1790 cm^{-1}). Addn. of 16.2 g. I with ice cooling to 18 g. Et_2NH in Et_2O over 0.5 hr., stirring 1 hr., followed by filtration and distn. under N_2 gave 81% 1-diethylaminoperfluoro-1,3-butadiene, b_{15} 45°, 1.3960, -, containing 9.29% hydrolyzable F (infrared spectrum has bands at 1710 and 1800 cm^{-1}). This shaken in Et_2O with H_2O a few minutes gave 86% $CF_2{:}CFCFHCONEt_2$, $b_{3.5}$ 63.5°, 1.4110, 1.2428 (infrared spectrum has bands at 1660 and 1800 cm^{-1}). Reaction of I with piperidine in Et_2O, run as above, gave after an aq. treatment 48% $CF_2{:}CFCFHCON(CH_2)_5$, b_5 94°, 1.4420, 1.3203 (infrared spectrum has bands at 1660 and 1800 cm^{-1}). Similar reaction of I with $EtNH_2$ in Et_2O gave after treatment with ice-HCl a low yield of $EtNHCOCF{:}CHCONHEt$, m. 195° (from Et_2O) and a little $CF_2{:}CF{-}CFHCONHEt$, m. 55-56° (from octane).

G.M.Kosolapoff.

aq. KI gave after a steam distn. 80.9% 2,4-difluoroiodobenzene, b. 175-6°, b_{25} 75°, n_D^{20} 1.5574. Bromination of m-$C_6H_4F_2$ in the presence of Fe gave after 1 day at room temp. 70.7% 2,4-difluorobromobenzene, b. 145-46°, n_D^{20} 1.5059. This was converted to the Grignard reagent by reaction with Mg in the presence of equimolar amount of EtBr by entrainment method; the soln. was treated with $CoCl_2$ under H_2 and finally treated with CH_2:$CHCl$ at 0°, warmed to room temp. for 2 hrs. and quenched in ice-HCl, yielding 5% 2,4-difluorostyrene which was isolated only as the dibromide, which was identical with the one described above, b_{10} 111-15°.

G.M.Kosolapoff.

2. 2,4-Difluoro-β-fluorostyrene and 2,4-difluoro-ββ-difluorostyrene. Organic Ibid. 71-75.

Bromination of 2,4-difluoroacetophenone at 0°, finally 4 hrs. at room temp., gave 90.7% 2,4-difluoro-β,β-dibromoacetophenone, b_2 104-105°. This (62.8 g) was added dropwise over 3 hrs. at 160° and 16 mm. to a soln. prepd. from 31.8 g. KF and 170 ml. dry glycerol (heated 0.5 hr. at 160° under gradually improving vacuum); further heating to 185° at 9-10 mm. gave a distillate of 10% 2,4-difluoro-β,β-difluoroacetophenone, b_{25} 91-92°, n_D^{20} 1.4694; this was obtained in 48.3% yield by treatment of 2,4-$F_2C_6H_3Br$ in Et_2O at -75° with ethereal BuLi soln., followed by F_2CHCO_2H, stirring 10 min. and quenching in ice; the product, b_{25} 90-90.5°, n_D^{20} 1.4694. Reduction of this with $NaBH_4$ in aq.NaOH-MeOH gave after 1 hr. at under 50° and quenching in aq. NaOH, 90.2% 2,4-difluorophenyldifluoromethylcarbinol, b_{24} 105°, n_D^{20} 1.4582, which with $SOCl_2$-pyridine at below 25°, finally 1 hr. at 80°, gave after an aq. treatment 78.8% 2,4-$F_2C_6H_3CHClCHF_2$, b_{25} 81-82°, n_D^{20} 1.4606. This (13.3 g.) heated carefully with 0.35 g. powd. Cu, 6.15 g. Zn dust and 86 g. $AcNH_2$ to 85°, then 120° 0.5 hr. gave after quenching in aq. [illegible] 88.2% 2,4-$F_2C_6H_3CH$:CHF, b_{40} 65-67°, n_D^{20} 1.4800. Reaction of 250 ml. [illegible] BuLi in Et_2O with 38.6 g. 2,4-$F_2C_6H_3Br$ and 13 g. F_2CHCO_2H as above gave 45% 2,4-$F_2C_6H_3COCHF_2$, b_{35} 98-99.5°, n_D^{20} 1.4685; the same formed in 22.5%

yield from m-$C_6H_4F_2$ and AcCl, in the presence of $AlCl_3$, in CS_2; b_{38} 94-95°, n_D^{20} 1.4685, along with a fraction, b_{43} 64-65.5°. The ketone treated with $NaBF_4$ in aq.NaOH-MeOH gave 83.7% 2,4-$F_2C_6H_3CH(OH)CCl_2F$, b_{35} 112-113.5°, n_D^{20} 1.4642, which with pyridine-$SOCl_2$, finally at 78-80° 0.5 hr., gave 57.7% 2,4-$F_2C_6H_3CHClCCl_2F$, b_{35} 95-97°, n_D^{20} 1.4589, which heated with Zn dust in $AcNMe_2$ at 120-30° 2.5 hrs. gave after quenching in aq. H_2SO_4 and extn. with Et_2O, 38.2% 2,4-$F_2C_6H_3CH:CF_2$, b_{60} 62°, n_D^{20} 1.4545.

G.M.Koselapeff.

Organic

Condensation of vinylcyclohexene with propiolic and tetrolic acids and their esters.

I. N. Nazarov, S. N. Ananchenko and I. V. Torgov (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 95-102.

Stirring 500 g. 1,3-dichloro-2-butene with 1 l. H_2O and 380 g. powd. $CaCO_3$ 12 hrs. at 70-80° gave after extn. with Et_2O 61% 3-chloro-2-buten-1-ol, (I), b_{12} 65-69°, n_D^{20} 1.4650. To 200 g. powd. KOH in 320 ml. abs. EtOH was added at room temp. with stirring 250 g. I and after 4.5 hrs. at 100°, standing overnight, diln. with 300 ml. EtOH, neutralization with CO_2, filtration, acidification of the filtrate with HCl, refiltration and distn., there was isolated 71% 2-butyn-1-ol, b. 140-45°, n_D^{20} 1.4550. This (31 g.) in 220 ml. Me_2CO was treated over 1.5 hrs. with 63 g. CrO_3 in 30% H_2SO_4, stirred 5 hrs. and left overnight; after extn. with Et_2O, 48% tetrolic acid, m. 76-77°, b_{16} 96-100°, was isolated. This refluxed with MeOH in the presence of H_2SO_4 16 hrs. gave the Me ester, b_{85} 80-82°, n_D^{19} 1.4408. C_2H_2 was introduced into soln. of 46 g. Na in 1.5 l. liq. NH_3 until the color was discharged, after which 500 ml. Et_2O was added, NH_3 was evaporated, finally in N_2 stream, and the resulting suspension of $NaNH_2$ in Et_2O was treated with CO_2 at 25-30 atm. in autoclave 72 hrs. at room temp., yielding after aq. treatment and acidification 52% propiolic acid, b_{50} 80-88°, which with MeOH-H_2SO_4 in 2 days at room temp. gave the Me ester, b. 102°. Refluxing 4.5 g. 1-vinylcyclohexene (XI) with 3.7 g. Me propiolate in MePh 9 hrs. gave 86% (based on conversion) mixed Me $\Delta^{1,4}$-hexahydronaphthalene-1-carboxylate and -2-carboxylate, b_8 124-25°, n_D^{20} 1.5170, d_{20} 1.065. Refluxing 10.4 g. XI with 8 g. propiolic acid in dioxane 10 hrs. gave 5 g. pure $\Delta^{1,4}$-hexahydronaphthalene-1-carboxylic acid, m. 137-38°, λ_{max} 246 mμ; the mother liquor gave 5.5 g. crystals, m. 88-93°, of mixed acids which could not be sepd. and after many recrystallizations gave merely the constant melting mixture of the 1- and 2-carboxy isomers, m. 96-98°. Very slow

crystallization of this from petr. ether (very dil. soln.) gave the 1-carboxylic acid, needles, m. 136-37°, and the 2-carboxylic acid, plates, m. 129-30°, λ_{max} 246 mμ, which were sepd. mechanically. Hydrolysis of the mixed Me esters (above) with aq. NaOH gave the same isomeric acids, which were sepd. as above. Esterification of the 1-carboxylic acid with CH_2N_2 gave its Me ester, $b_{1.5}$ 91-1.5°, n_D^{22} 1.5145, which on saponification with aq. NaOH gave the original acid, m. 137-38°. Hydrogenation of the pure $\Delta^{1,4}$-hexahydronaphthalene-1-carboxylic acid over Pt in MeOH gave cis-syn-decahydronaphthalene-1-carboxylic acid, m. 124-25°; the same formed over Pd-$CaCO_3$, or over Pt in AcOH. The acid treated with $(COCl)_2$, followed by NH_3, gave the amide, m. 235-36°. Similar hydrogenation of $\Delta^{1,4}$-hexahydronaphthalene-2-carboxylic acid gave cis-trans-decahydronaphthalene-2-carboxylic acid, m. 80.5-81°; amide, m. 178-79° (from EtOH); the acid treated in $CHCl_3$ with H_2SO_4 and NaN_3, followed by BzCl in the presence of NaOH, gave the N-benzoylamide, m. 128-29°. Reduction of $\Delta^{1,4}$-hexahydronaphthalene-1-carboxylic acid with $LiAlH_4$ on Et_2O overnight gave after the usual treatment 76% 1-hydroxymethyl-$\Delta^{1,4}$-hexahydronaphthalene, m. 50-51°, which (1 g.) treated with 0.7 g. powd. K_2CO_3 and 0.6 g. PBr_3 in petr. ether at -70°, then at room temp. overnight, gave 1.2 g. 1-bromomethyl analog, a strong lachrymator, n_D^{20} 1.5480; this condensed with sodio-malonic and -acetoacetic esters, but the products were unstable; the reaction failed to go with sodioacetone. Heating 7.8 g. II with 7.8 g. Me tetrolate in dioxane 3 hrs. at 130° in autoclave gave 3.2 g. mixed condensation products, b_3 107-18°. This refluxed 10 hrs. with MeOH-KOH gave after acidification 0.4 g. 2-methyl-$\Delta^{1,4}$-hexahydronaphthalene-1-carboxylic acid, m. 165-66°; some dimer of II was also isolated, b_5 139-40°. Heating II with terolic acid in dioxane as above gave after recrystallization from Me_2CO a low yield of pure 2-methyl-$\Delta^{1,4}$-hexahydronaphthalene-1-carboxylic acid, m. 166.5-67°; Keeping 0.3 g. 1-vinyl-6-methoxy-3,4-dihydronaphthalene and 0.16 g. propiolic acid in dioxane 2 hrs., then refluxing 1 hr. gave 60% mixed acids which after separn. from dioxane-Et_2O gave

Organic

Synthesis of methylolcrotonamide.

S. N. Ushakov, E. M. Lavrent'eva and K. S. Podgorskaya (HighnPolymer Inst., Leningrad). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 91-94. The following conditions were found to be best from the synthesis of methylolcrotonamide. Equimolar amounts of crotonamide and paraformaldehyde were made to react in the presence of 2.5-3% EtONa at 68-70° 15-20 min. in CCl_4 soln. with stirring; the upper layer was sepd., filtered and chilled overnight, yielding 62-85% MeCH:CHCONHCH$_2$OH, needles, m. 87° (from EtOAc or C_6H_6), n 1.5160. Heated in aromatic solvent with distn. of H_2O with the solvent vapors it formed the ether (MeCH:CHCONHCH$_2$)$_2$O, m.136°, n_e^{20} 1.5557, n 1.5540, d_{20}^{20} 1.1312.

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Organic

Organic

Addition of thioacetic acid to alkenyltrialkylsilanes and the synthesis of silicon-containing mercaptans.

V. F. Mironov and N. A. Pogonkina (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 85-90. Cf. 1956, 707. AcSH adds contrary to the Markovnikov rule to unsatd. radicals of silanes. $Me_2EtSiCl$ and $CH_2:CHCH_2I$ added simultaneously to Mg in Et_2O and heated 5 hrs. gave 21% $Me_2EtSiCH_2CH:CH_2$, b. 110-16°, b_{760} 116°, n_D^{20} 1.4219, d_{20} 0.7435. Similarly was prepd. 50% $Me_2PrSiCH_2CH:CH_2$, b_{760} 137°, 1.4271, -. Keeping 23 g. $Me_2SiCH_2CH:CH_2$ and 16 g. AcSH overnight gave 78.5% $Me_2Si(CH_2)_3SAc$, b_{12} 92°, 1.4655, 0.9198. Similarly were obtained: 60% $Me_2EtSi(CH_2)_3SAc$, b_8 99°, 1.4706, 0.9226; 75.6% $Me_2PrSi(CH_2)_3SAc$, b_2 78°, 1.4702, 0.9148; 82.6% $Me_2PhSi(CH_2)_3SAc$, b_2 121°, 1.5311, 1.0129; $Et_3Si(CH_2)_3SAc$, 84.7%, b_5 122°, 1.4785, 0.9274; 87.8% $EtMe_2SiCH_2CHMeSAc$, b_5 80°, 1.4743, 0.9383; 81.1% $Me_2EtSi(CH_2)_4SAc$, b_1 86°, 1.4699, 0.9181; 96% $MeEt_2Si(CH_2)_4SAc$, b_1 95-94°, 1.4740, 0.9211; $Me_2PrSiCH_2CH_2SAc$, 67%, b_6 82-84°, 1.4660, 0.9308. To 11 g. $Me_3SiCH:CH_2$ and 14.1 g. $Me_3SiCH_2CH_2CH:CH_2$ was added 1.1 mole AcSH and after 2 days this gave some unreacted materials and 31% adduct of the vinyl silane and 51% that of the butenyl silane. Refluxing 70 g. KSCN and 97.5 g. $Me_3SiCHMeCl$ and 400 ml. EtOH 45 hrs. gave 35% $Me_3SiCHMeSCN$, b_6 98°, 1.4713, 0.9414. This (40 g.) and BuMgBr from 110 g. BuBr gave 86% [illegible] $Me_3SiCHMeSH$, b_{43} 50-56°, which with $CH_2:CHCN$ gave 61.2% $Me_3SiCHMeSCH_2CH_2CN$, b_7 157°, 1.4879, 0.9336. Similarly were prepd.: 55% $Me_3SiCH_2CH_2SH$, b_{45} 62-63°, 1.4540, 0.8488; 63% $Me_3Si(CH_2)_3SH$, b_{50} 97°, 1.4559, 0.8496; 72.4% $Et_3Si(CH_2)_3SH$, b_5 82°, 1.4738, 0.8794; 73.8% $Me_2PhSi(CH_2)_3SH$, b_2 110°, 1.5388, 0.9755; 72.1% $Me_2PrSi(CH_2)_3SH$, b_2 80°, 1.4630, 0.8596; 47.5% $Et_2MeSi(CH_2)_4SH$, b_6 89.5°, 1.4690, 0.8716; 51.4% $EtMe_2Si(CH_2)_4SH$, b_6 73.5°, 1.4656, 0.8625. To 5 g. NaOH and 27 ml. H_2O and 12 ml. EtOH was added 23 g. $Me_3Si(CH_2)_3SMe$, yielding after 5 hrs. reflux 63% $Me_3Si(CH_2)_3SH$; the mercapto derivs. above were prepd. by this method from the thioacetates. To $Me_3Si(CH_2)_3SH$ was added 2 drops MeONa-MeOH followed by 14 g. $CH_2:CHCN$ at 70°, yielding after washing 79% $Me_3Si(CH_2)_3SCH_2CH_2CN$, b_3 148°, 1.4767, 0.9286. Similarly were prepd.:

80.2% $Me_3Si(CH_2)_3SCH_2CH_2CN$, b_6 147-48°, 1.4774, 0.9371; 84.8% $Et_3Si(CH_2)_3SCH_2CH_2CN$, b_5 152°, 1.4869, 0.9565; 83% $PrMe_2Si(CH_2)_3SCH_2CH_2CN$, b_3 139°, 1.4790, 0.9241; 79.9% $Me_2PhSi(CH_2)_3SCH_2CH_2CN$, b_9 208°, 1.5360, 1.-144; 97% $EtMe_2Si(CH_2)_4SCH_2CH_2CN$, b_6 153.5°, 1.4602, 0.9251; 72% $MeEt_2Si(CH_2)_4S-CH_2CH_2CN$, b_5 168.5°, 1.4823, 0.9278; MeCl passed into Et_2O with 75 g. Mg 16 hrs., followed by addn. of 252 g. $MeSiCl_2CH_2CH_2CH_2Cl$ and reflux 8 hrs. gave after an aq. treatment 83.4% $ClCH_2CH_2CH_2SiMe_3$, b_{740} 150°, 1.4320,-. This with EtSNa in Et_2O gave in 40 hrs. 74.3% $Me_3Si(CH_2)_3SEt$, b_7 70-71°, 1.4581, 0.8479. The same formed from $Me_3SiCH_2CH{:}CH_2$ and EtSH in 10 days' standing (60.5%). Hydrolysis of $Me_3SiCH_2CHMeSP(S)(OMe)_2$ gave $Me_3SiCH_2CHMeSPO$ whose infra-red spectrum was quite different from that of the above isomer. Trialkylalkenylsilanes and S yield mixed polysulfides.

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Emanating ability in topochemical processes as a characterization of specific surface.

M. D. Sinitsyna, G. M. Zhabrova, S. Z. Roginskii and V. A. Gordeeva, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 176-78.

A specimen of $Mn(OH)_2$ containing radiothorium was subjected to heating from 320° to 1080° with detn. of evolved H_2O and estn. of the emanating ability by detn. of the evolved thoron. It was shown that a linear dependence exists between the emanation coeff. and the specific surface of the specimen used. This suggests the use of such procedures for estn. of specific surfaces of solids in place of the sorptional methods.

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Organic

Polymerization of vinyl- and allyl derivatives of IV group elements. V. V. Korshak, A. M. Polyakova, V. F. Mironov and A. D. Petrov (Inst. Hetero-org. Comds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 178-80.

Cf. this j. 1956, 980, and Zhur. Obshch. Khim. 27, 2445 (1957). Heating $Me_3SiCH{:}CH_2$ 6 hrs. at 120° under 6000 atm. in the presence of $(Me_3CO)_2$ gave a liquid polymer of low mol. wt., comparable to that formed by $Me_3CCH{:}CH_2$. $Me_3SiCH_2CH{:}CH_2$ also gave a low mol. wt. polymeric oil; $Me_3GeCH{:}CH_2$ gave a similar result as did $Me_3GeCH_2CH{:}CH_2$ and $Et_3SnCH{:}CH_2$. $Et_3SnCH_2CH{:}CH_2$ failed to polymerize, while $Me_{2}Et_2Ge(CH{:}CH_2)_2$ gave a good yield of tridimensional glassy polymer. Under the same conditions copolymers were formed from styrene and $Me_3GeCH_2CH{:}CH_2$, and $CH_2{:}CHCO_2Me$ and $Me_3SnCH_2CH{:}CH_2$ or $Me_3GeCH_2CH{:}CH_2$. Among vinyl and allyl derivs., those of Si polymerize better than do those of C, Ge or Sn; for derivs. of thiocyanate radical and the above elements, the ease of polymerization rises steadily from C to Si to Ge and to Sn, respectively.

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Organic

Hetero-chain polymeric esters. 12. Polyesters of azobenzene-3,3'- and 4,4'-dicarboxylic acids.

V. V. Korshak and S. V. Vinogradova (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 148-53. Cf. this j. 1957,000. Esterification of (:NC$_6$H$_4$CO$_2$H-m)$_2$ with MeOH-HCl gave the di-Me ester, 20%, m. 161-63°. The p-isomer failed to react under these conditions and required the reaction of the acyl chlorides with MeOH; the di-Me ester, m. 240-41°, was obtained in unstated yield. These esters were polycondensed in the presence of LiOH with aliphatic glycols ranging from C_2 to C_{20}, including also propylene glycol and diethylene glycols. The polyesters from the m,m'-isomer were generally low-melting solids, while those from the p,p'-isomer generally melted well above 150°. The polyesters from the m-isomer could be drawn into filaments, while those from the p-isomer could not. The range of m.pts. of the resulting polyesters is discussed at length from the viewpoint of electronic organic theory.

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13. Polyesters of p-xylylene glycol.

Ibid. 154-161.

Organic

Polyesters were prepd. from p-C$_6$H$_4$(CH$_2$OH)$_2$ and dicarboxylic acids: oxalic through sebacic, as well as hexadecanedioic, diglycolic, thiodivaleric, sulfonyldivaleric, isomeric C$_6$H$_4$(CO$_2$H)$_2$, diphenyldicarboxylic, diphenic, 2,5-dimethylterephthalic, diphenylmethane-3,3'- and 4,4'-dicarboxylic, diphenylketo-4,4'-dicarboxylic, p-phenylenediacetic, and trans- and cis-hexahydroterephthalic acids. These were solids whose m.pts. ranged up to over 340° for the terephthalic acid ester from as low at 38° for cis-hexahydroterephthalic acid ester. The necessary glycol was prepd. by hydrolysis of the bromide with aq. K$_2$CO$_3$. The polyesterifications were run with 0.3-0.5% LiOH as the catalyst. The M.pts. and solvs. of the products are tabulated and compared with each other at some length.

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Organic

Synthesis of organomercury nitro compounds.

S. S. Novikov, T. I. Godovikova and V. A. Tartakovskii (N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk SSSR, 124, 834-37 (1959). It was shown that $Hg[C(NO_2)_3]_2$ readily mercurates compds. with active H in Et_2O, H_2O, C_6H_6, EtOH, or MePh at 20-80°, the reaction being quite rapid in most cases, or requiring up to 60 hrs. for less reactive cases. The products are evidently $RHgC(NO_2)_3$ (R shown): $CH(CO_2Et)_2$, dec. above 250°; $AcCHCO_2Et$, m. 159°; O_2NCHCO_2Et, m. 135°; $CH(CO_2Me)_2$, m. 155°; $AcCH_3$, m. 155°; cyclopentanonyl, m. 140°; Ph, 146°, $MeOC_6H_4$ (p-, m. 149°; o-, m. 126°); $MeOC_6H_4$ (p-, m. 101°; o- m. 114°); PhNH, m. 117°; $p\text{-}Me_2NC_6H_4$, m. 110°; furyl, m. 120°; thienyl, m. 115°. With Br_2 these give $BrC(NO_2)_3$ and corresponding mercurobromides; concd. HCl yields RHgCl and $HC(NO_2)_3$. The spectra of the products depend on the solvent polarity indicating the possible existence in 2 tautomeric forms in soln. Reaction with aryl nitro compounds does not yield such products but rather adducts, such as: $O_2NPh.Hg[(C(NO_2)_3]_2$, m. 116°; $m\text{-}(O_2N)_2C_6H_4.Hg[C(NO_2)_3]_2$, m. 147°; $o\text{-}Me(O_2N)\text{-}C_6H_4.Hg[C(NO_2)_3]_2$, m. 75°; $o\text{-}MeO(O_2N)C_6H_4.Hg[C(NO_2)_3]_2$, m. 109°. Alkalies destroy these complexes and give the original nitroaromatic compd., HgO and salt of $CH(NO_2)_3$. Products of neither nature are formed from m-substituted nitro compounds, this indicating that the above complexes are additively linked at m-position relative to NO_2. Reaction of $Hg[C(NO_2)_3]_2$ with C_2H_4 in aq. or alc. medium gave $(O_2N)_3CCH_2CH_2HgC(NO_2)_3$; the same forms in $MeNO_2$ or $PhNO_2$ soln. Reaction with phenylcyclopropane gave $PhCH(CH_2)CH_2CH_2HgC(NO_2)_3$, while reaction with $EtOCH{:}CH_2$ gave $(O_2N)_3CHgCH_2CHO$ m. 128°, 65%. $RHgC(NO_2)_3$ also add to the double bonds. Thus were prepd.: $(O_2N)_3CCH_2CH_2HgC(NO_2)_3$, 95%, m. 167°; $(O_2N)_3CCH_2CH_2HgCl$, 92%, m. 142°; $(O_2N)_3CCH_2CH_2)_2Hg$, m. 155°; $(O_2N)_3CCHMeCH_2HgC(NO_2)_3$, 97%, m. 134°; $[(O_2N)_3CCHMe\text{-}CH_2]_2Hg$, 79%, m. 124°; $(O_2N)_3CCHPhCH_2HgC(NO_2)_3$, m. 129°, 80%; $o\text{-}(O_2N)_3CC_6H_4\text{-}HgC(NO_2)_3$, 55%, m. 95°; $[(O_2N)_3CCH(CH_2OH)CH_2]_2Hg$, 70%, m. 109°; and $(O_2N)_3C\text{-}CH_2CH(CO_2Me)HgC(NO_2)_3$, 82%, m. 150°. Iso-olefins do not add these Hg salts.

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Organic

Exchange reactions of isopropenyl compounds of mercury, thallium and tin. A. N. Nesmeyanov, A. E. Borisov and N. V. Novikova. (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 259-62. Exchange reactions of isopropenyl derivs. of Hg, Tl and Sn are described. Rapid heating of 5 g. $(CH_2:CMe)_2TlBr$ and 10 g. $SnBr_2$ at 200° gave a distillate of 75% malodorous liquid, which on redistn. gave 2.2 g. $(CH_2:CMe)_2SnBr_2$, b_{10} 100-101°, n_D^{20} 1.5665, d_{20} 1.9363. Stirring 3 g. $(CH_2:CMe)_2TlBr$ and 6 g. $SnBr_2$ in 50 ml. Me_2CO 5 hrs. at room temp. and 3 hrs. at 50° gave a ppt. which was sepd. Concn. of the filtrate gave 0.38 g. original $(CH_2:CMe)_2TlBr$. The residual liquid, after concn., was extd. with petr. ether and the ext. treated with 20% KOH, the resulting solid being treated with 15% HBr; this treatment yielded an unstated amount of $(CH_2:CMe)_2SnBr_2$, b_9 102.5°, n_D^{20} 1.5664. The original ppt. was identified as TlBr (73%). Stirring 3 g. $(MeCH:CH)_2TlBr$ and 6 g. $SnBr_2$ in C_6H_6 6 hrs. at 50° gave among undescribed products, some 1.1 g. $(MeCH:CH)_2SnBr_2$, b_{10} 121-22°, n_D^{20} 1.5663. To 1 g. $(CH_2:CMe)_2SnBr_2$ in 5 ml. EtOH was added 2 g. $HgBr_2$ in 5 ml. EtOH and 10 ml. H_2O; after brief heating and addn. of 15 ml. H_2O, followed by 12 hrs. standing, there was obtained 43% $(CH_2:CMe)HgBr$, m. 167° (from Me_2CO). To 1 g. $(CH_2:Me)_2SnBr_2$ in 10 ml. MeOH was added 15 ml. 20% NaOH which dissolved the originally formed solid; the mixture was treated with 1 g. $HgBr_2$ in 10 ml. MeOH and kept 2 hrs. after which it was extd. with Et_2O, the ext. yielding 79% liquid $(CH_2:CMe)_2Hg$, which with $HgBr_2$ in Me_2CO gave $CH_2:CMeHgBr$, m. 166-67°. To 1 g. $(CH_2:CMe)_2Hg$ in Et_2O was added 0.8 g. $TlBr_3$ in Et_2O; after 1 hr. the thickened mixt. was treated with 20 ml. C_6H_6, warmed on a steam bath and filtered; this gave 89% $(CH_2:CMe)_2TlBr$, dec. 190-94°, while the evapd. filtrate gave 70% $CH_2:CMeHgBr$, m. 167°. Stirring 5.9 g. $(CH_2:CMe)_2Hg$ and 12 g. $SnBr_2$ in petr. ether 5 hrs. and washing the sepd. ppt. with petr. ether and Me_2CO gave on evapn. of the Me_2CO soln. 1.72 g. $CH_2:CMeHgBr$; the petr. ether soln. gave a liquid which treated with 20% KOH and the resulting solid treated with 15% HBr, gave some $(CH_2$

some $(CH_2:CMe)_2SnBr_2$ while the alkaline soln. on extn. with Et_2O gave 0.6 g. $(CH_2:CMe)_4Sn$, b_8 66-67°, n_D^{20} 1.5110, d_{20} 1.3153; and 44% Hg was also isolated. Reaction of 4 g. $(CH_2:CMe)_2Hg$ with 8 g. $SnBr_2$ in 20 ml. petr. ether 5 hrs. at 65° gave 1.03 g. $CH_2:CMeHgBr$, 1.1 g. $(CH_2:CMe)_2SnBr_2$, 0.4 g. $(CH_2:CMe)_4Sn$ and 2.05 g. Hg. To 1 g. $(CH_2:CMe)_2Hg$ in 5 ml. Me_2CO was added 2 g. $SnBr_2$ in 10 ml. Me_2CO yielding a ppt. of Hg immediately; after 20 hrs. at room temp. there was isolated: 0.57 g. $CH_2:CMeHgBr$, 0.22 g. $(CH_2:CMe)_2SnBr_2$, 0.2 g. $(CH_2:CMe)_4Sn$ and 0.32 g. Hg. To 1 g. $(CH_2:CMe)_2Hg$ was added 2 g. powd. $SnBr_2$ (somewhat exothermic) and after 20 hrs. at room temp., the mixt. gave 0.42 g. $CH_2:CMeHgBr$, 0.1 g. $(CH_2:CMe)_2SnBr_2$, 0.3 g. $(CH_2:CMe)_4Sn$ and 0.35 g. Hg.

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Organic

Synthesis of organo-tin compounds from organomercury compounds and salts of divalent tin in inert solvents.

A. N. Nesmeyanov, A. E. Borisov, N. V. Novikova and M. A. Osipova. (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 263-66. Cf.J.Rus.Phys.Chem.Soc. 62, 1796(1931).

Stirring 5.9 g. $(CH_2:CMe)_2Hg$ and 12 g. $SnBr_2$ in 30 ml. petr. ether 5 hrs., sepg. the ppt. and washing it with petr. ether then with Me_2CO gave on evapn. of the Me_2CO soln. 1.72 g. $CH_2:CMeHgBr$. Evapn. of the petr. ether soln. gave a liquid which treated with 20% KOH gave a ppt. which with 15% HBr gave 22% $(CH_2:CMe)_2SnBr_2$, b_9 102.5°, n_D^{20} 1.5667, d_{20} 1.9360; the alkaline soln. on extn. with Et_2O gave 0.6 g. $(CH_2:CMe)_4Sn$, b_8 66-67°, n_D^{20} 1.5110, d_{20} 1.3153; the reaction also gave 1.86 g. Hg. Similar reaction run at 65° gave 71% Hg, 21% $(CH_2:CMe)_2SnBr_2$ and small amounts of $CH_2:CMeHgBr$ and $(CH_2:CMe)_4Sn$. Similar reaction in Me_2CO at room temp. also gave the same 4 products. Stirring 5 g. Et_2Hg and 7 g. $SnCl_2$ in ligroin 12 hrs. at 90° followed by sepn. of the ppt. and washing it with hot petr. ether and MeOH gave, from petr. ether soln. 2.5 g. Et_2SnCl_2, m. 83-3.5°, while the MeOH

soln. gave ~~2x3Cxgx~~ 1 g. EtHgCl; 2.59 g. Hg was isolated. Powd. Ph_2Hg (3 g.) and 3 g. $SnCl_2$ in ligroin in 7 hrs. at 60-65° gave 1.66 g. Hg and 75% Ph_3-nCl, m. 102-104° (from petr. ether). Similarly 2 g. Ph_2Hg and 2 g. $SnBr_2$ in ligroin gave in 12 hrs. at 60-70° 0.27 g. Ph_3SnCl, 0.33 g. PhHgBr and .5 g. Hg. Similarly 3 g. $(p\text{-}MeC_6H_4)_2Hg$ and 3 g. $SnCl_2$ in ligroin in 13 hrs. at 90-5° gave after the above-described treatment, 72% $(p\text{-}MeC_6H_4)_2SnCl_2$, m. 49.5° (from petr. ether) and 1.51 g. Hg. Similarly $SnCl_2$ and $(o\text{-}MeC_6H_4)_2$-Hg gave 66% $(o\text{-}MeC_6H_4)_2SnCl_2$, m. 49.5-50° and 100% Hg. Similarly 3.8 g. $(1\text{-}C_{10}H_7)_2Hg$ and 4 g. $SnCl_2$ in 20 hrs. at 90-5° gave 53% $(1\text{-}C_{10}H_7)_2SnCl_2$, m. 130-32°(crude), m. 136-37° (from petr. ether), and 95% Hg.

G.M.Kosolapoff.

Organic

Fluorinated styrenes. 3. Styrenes, fluorinated in the side chain.
M. M. Nad, T. V. Talalaeva, G. V. Kazennikova and K. A. Kocheshkov. ~~Ix~~ (L. Ya. Karpov Phys. Chem. Inst., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 272-77. Cf. Cohen et al. JACS 71, 3439 (1949) and Prober JACS 75, 968(1953). No ref. given to parts 1 and 2.

A convenient low temp. organolithium route was developed for the synthesis of fluoroacetophenones. Under N_2 atm. 240 ml. 1.42 N Et_2O soln. of PhLi was cooled to -72° and treated dropwise with 11.2 g. CHF_2CO_2H in 30 ml. Et_2O over 35 min.; after stirring 2 hrs. at -75°, the mixture was poured on ice-HCl and extd. with Et_2O, yielding 67% CHF_2COPh, b_{26} 83.5-84°, n_D^{20} 1.4984. Heating 95 g. KF in 250 ml. dry glycerol at 170-75° at 16-17 mm with gradual application of vacuum was then followed by addn. of $CHCl_2COPh$ (94 g.) over 4 hrs. at 158-63°; distn. began after 40-50 min. and after gradual heating to 190° at 6-8 mm. there was obtained 32-6% CHF_2COPh. The ketone (31.2 g.) in 1 vol. MeOH was added over 15 min. to a soln. of 3.8 g. $NaBH_4$ in 25 ml. H_2O and 4 ml. 2N NaOH at 10° initially, 20-30° during the bulk of the addn.; after 1 hr. stirring, the mixt. was poured into 10% NaOH and extd. with Et_2O, yielding 92.4% $CHF_2CH(OH)Ph$, b_{20} 105°, n_D^{20} 1.4940. This with $SOCl_2$-pyridine at below 35°, then at 85-90° 0.5 hr., gave 82-86% $CHF_2CHClPh$, b_{25} 89-90°, n_D^{20} 1.4950. This, 41.1 g., mixed with 0.3 g. powd. Cu, 60 g. $AcNH_2$ and 22.8 g. Zn dust was heated gradually to 150° and kept 2 hrs. at 150-54°, then treated with dil. H_2SO_4 and extd. with Et_2O, yielding 60-65% $PhCH{:}CHF$, b_{50} 75-6.5°, n_D^{20} 1.5257. Similarly, PhLi and CF_2Cl-CO_2H gave 50% $PhCOCClF_2$, b_{35} 94-96°, 1.4950, which reduced with $NaBH_4$ to 90-5% $PhCH(OH)CClF_2$, b_5 85-6°; the result was the same in the reduction with $(iso\text{-}PrO)_3Al$-iso-PrOH. The carbinol was converted as above to $PhCHCl$-$CClF_2$, 78%, $b_{22.5}$ 91.5-93°, which as above gave 60-77% $PhCH{:}CF_2$, b_{62} 65-66°, 1.4927; this gives a dibromide, which with Zn dust in $AcNH_2$ again gave the original $PhCH{:}CF_2$. PCl_5 and $PhCOCHF_2$ gave 85% $PhCCl_2CHF_2$, b_{30} 105.5-107°, n_D^{30} 1.5045, n_D^{20} 1.5086. This with SbF_3 gave 35-40% $PhCClFCHF_2$, b_{55} 92-94°,

n_D^{20} 1.4683. This with Zn-Cu-$AcNH_2$ as above at 125-30° gave 43% PhCF:CHF, b_{60} 88-90°, 1.5060. Heating 128 g. $PhCOCHCl_2$ with 176 g. PCl_5 0.5 hr. at 145° and 8 hrs. at 175° gave 37% $PhCCl_2CHCl_2$, b_3 120-22°, which (61 g.) was heated with 45.5 g. SbF_3 and 1 ml. Br_2 under 10-11 mm. with slow distn. of products, yielding 46% $PhCF_2CHCl_2$, b_{10} 84°, 1.5000, which heated as above with Zn-Cu-$AcNH_2$ at 150° 2 hrs. gave 81% PhCF:CHCl, b_{14} 86-87°, 1.5531.

G.M.Kosolapoff.

Organic

Reaction of -chloromethylethoxysilanes with amines.

K. A. Andrianov and L.M.Volkova (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 277-82.

It was shown that amines react at 20° with silanes contg. the CH_2Cl group and EtO groups, the rates being dependent on the amine. The following series of descending reactivity was established on the basis of kinetic curves which are shown: $HOCH_2CH_2NH_2$, $Me_3SiOCH_2CH_2NH_2$, $EtNH_2$, Et_2NH, $PhNH_2$, EtPhNH, and: $ClCH_2SiMe_2OEt$, $ClCH_2SiMe(OEt)_2$, $ClCH_2Si(OEt)_3$. Keeping 35 g. $ClCH_2SiMe_2OEt$ with 50 g. $EtNH_2$ 15 days at 20° gave 65% $EtNHCH_2SiMe_2OEt$, b_{751} 163.5-54.5°, n_D^{20} 1.4149, d_{20} 0.8358. Similarly $ClCH_2SiMe(OEt)_2$ gave 56% $EtNHCH_2SiMe(OEt)_2$, b_{757} 180-81°, 1.4120, 0.8870. Keeping 18.2 g. $ClCH_2SiMe(OEt)_2$ and 37 g. $PhNH_2$ in 18 g. abs. EtOH 15 days gave 13.5% $PhNHCH_2SiMe(OEt)_2$, b_5 125-30°, 1.4990, 1.010. The kinetic curves which are shown were obtained by reactions run at 20° with the appropriate silanes, amines and EtOH, the latter being used to dissolve the resulting amine salts.

G.M.Kosolapoff.

New methods of synthesis of organosiloxanes.

N. F. Orlov and B. N. Dolgov (Silicate Chem. Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 125, 817-20 (1959).

Heating 10.2 g. $MeEt_2SiH$ and 18 g. Ph_3SiOH in C_6H_6 with 0.001 g. colloidal Ni 7 hrs. gave 1.5 l. H_2 and 86% $MeEt_2SiOSiPh_3$, b_5 212°, d_{20} 1.0304, n_D^{20} 1.5580. Similarly was prepd. 72% $MeEt_2SiOSiEt_3$, b_{763} 208-9°, 0.8323, 1.4240; 74.3% $Et_3SiOSiPh_3$, b_2 205°, 1.0275, 1.5581; 80% $MePr_2SiOSiPh_3$, $b_{3.5}$ 207°, 1.0123, 1.5500; 78.3% $EtPr_2SiOSiPh_3$, $b_{2.5}$ 208°, 1.0118, 1.5490. Similar use of $Ph_2Si(OH)_2$ with appropriate silanes gave: 48% $(MeEt_2SiO)_2SiPh_2$, b_3 185°, 0.9704, 1.4930; 75% $(MePr_2SiO)_2SiPh_2$, $b_{2.5}$ 190°, 0.9762, 1.5024; 76% $(Et_3SiO)_2SiPh_2$, b_3 194°, 0.9768, 1.5012. Also listed are: $(Et_3SiOSiEt_2)_2O$, 71.2%, b_4 172°, 0.9064, 1.4390; $MePr_2SiOSiPr_2Me$, 74%, b_4 99°, 0.8249, 1.4285; $(MePh_2Si)_2O$, 83%, m. 49°, b_6 203°; $(MeEt_2Si)_2O$, b_{760} 192°, 0.8212, 1.4185, and $(Et_3Si)_2O$, b_{760} 233°, 0.8457, 1.4330. Heating 20 g. $MePh_2SiH$ with 0.02 g. $NiCl_2$ 10 min. until colloidal Ni formed, followed by cooling, addn. of 30 ml. MePh and 1.8 ml. H_2O and heating again 4 hrs. gave 2.3 l. H_2 and 83% $(MePh_2Si)_2O$. The condensation described above evidently occurs through reaction of the silane with H_2O formed by dehydration of the silanols.

G.M.Kosolapoff,

Individual hydrocarbons of cyclohexane series from gasoline fractions of Sakhalin petroleum.

N. I. Podkletnov (Sakhalin Res.Inst., Acad.Sci.). Doklady Akad. Nauk S.S.S.R. 125, 821-2 (1959).

Examn. of Sakhaline petroleum gasoline fractions showe the presence of the following cyclohexane derivs.: methylcyclohexane, cyclohexane, ethylcyclohexane, 1,2- and 1,3-dimethylcyclohexanes, these groups accounting for 64-74% of the total fractions. Also found in smaller amounts were 1,4-dimethylcyclohexane, propyl- and isopropylcyclohexanes, 1,2-, 1,3-, and 1,4-methylethylcyclohexanes, 1,2,3-, 1,2,4- and 1,3,5-trimethylcyclohexanes, perhydroindane.

G.M.Kosolapoff.

Organic

Synthesis of polymerizable methacrylates of trialkyl(aryl)tin.

M. M. Koton, T. M. Kiseleva and V. A. Paribok (High Polymer Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 125, 1263-4 (1959).

The conventional conversion of R_4Sn to R_3SnCl and to R_3SnOH gave: Me_3SnOH, needles; Et_3SnOH, b_{20} 153-5°, m. 45°; and Bu_3SnOH, b_5 186-90°, as well as Ph_3SnOH, m. 119°. These and equimolar amt. of $CH_2:CMeCO_2H$ were heated 0.5-1.0 hr. in Me_2CO and distd., yielding 60-80% corresponding methacrylates: $Me_3SnO_2CCMe:CH_2$, m. 122°; tri-Et analog, m. 76-9°; tri-Bu analog, m. 20-2°; tri-Ph analog, m. 91-2° (with alc. HCl this gave the free acid and Ph_3SnCl). Alc. KOH gave $CH_2:CMeCO_2K$ and Ph_3SnOH. The esters polymerize both in the absence of added catalysts and with peroxides and azo compds.

G.M.Kosolapoff.

Organic

Polymerization of vinylaromatic organosilicon compounds. Derivatives of α-methylstyrene.

V. V. Korshak, A. M. Polyakova, A. A. Sakharova, A. D. Petrov and E. A. Chernyshev (Inst. Hetero-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 791-3 (1959).

Polymerization of $R_3SiC_6H_4CMe{:}CH_2$-p was run either with $(Me_2C(CN)N{:})_2$ at 80° or $(Me_3CO)_2$ at 130° under 600 atm. (no polymerization occured without pressure) 6 hrs. and glassy polymers were obtained from monomers with p-substituents of: Et_3Si, Et_3SiCH_2, $Et_3SiCH_2CH_2$, and Me_3SiCH_2. The nitrile was the more effective catalyst. Characteristic viscosities and thermomechanical properties of the polymers are shown graphically. In general, viscosities decrease in passing from $PhCMe{:}CH_2$ to $Et_3SiC_6H_4$-$CMe{:}CH_2$ and to the more complex polymers. For synthesis of the monomers see Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, no pp. given (Petrov, Chernyshev and Tolstyakova).

G.M.Kosolapoff.

Organic

Addition reaction of trialkoxysilanes to olefins.

N. S. Nametkin, A. V. Topchiev, T. I. Chernysheva and L. I. Kartasheva (Petrochem.Synth. Inst., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 794-7 (1959). cf. US Pat. 2,637,737; C.A. 8254 (1954).

Addn. of 24.6 g. $(EtO)_3SiH$ to 18.9 g. 1-nonene and 1 ml. chloroplatinic acid soln. at 100-10° and heating 2-3 hrs. gave 41.4% $C_9H_{19}Si(OEt)_3$, b_2 130-3°, n_D^{20} 1.4182, d_{20} 0.8827. Similarly were obtained: 18.2% $C_8H_{17}Si(OCMe_3)_3$, b_2 138-40°, 1.4200, 0.8650; $C_8H_{17}Si(OBu)_3$, 21.1%, b_2 155-8°, 1.4280, 0.8747 64.9% $C_9H_{19}Si(OCHMe_2)_3$, b_2 128-32°, 1.4180, 0.8589; 43.1% $C_9H_{19}Si(OBu)_3$, b_2 164-6°, 1.4298, 0.8715; 37.8% $C_9H_{19}Si(OCHMeEt)_3$, b_2 160-4°, 1.4270, 0.8714; 12.5% $C_9H_{19}Si(OCMe_3)_3$, b_2 150-5°, 1.4232, 0.8622; 78.4% $C_9H_{19}Si$-$(OCH_2CHMe_2)_3$, b_4 175-6°, 1.4260, 0.8700; 65.2% $C_{10}H_{21}Si(OBu)_3$, b_2 167-70°, 1.4315, 0.8710; and 20.5% $C_{10}H_{21}Si(OCMe_3)_3$, b_2 160-1°, 1.4260, 0.8589. The addn. occurs contrary to Markovnikov rule. G.M.Kosolapoff.

Organic

Synthesis of triethylsiloxy derivatives of vanadium and antimony.

K. A. Andrianov, A. A. Zhdanov and E. A. Kashutina (Inst. Hetero-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1261-3 (1959).

To 37.5 g. Et_3SiONa in 200 ml. C_6H_6 was added dropwise 14 g. $VOCl_3$ in 50 ml. C_6H_6 over 40 min.; after filtration there was obtained 60% pale yellow $(Et_3SiO)_3VO$, $b_{3.5}$ 186.5°, d_{20} 0.9816, n_D^{20} 1.4820. Similarly $SbCl_3$ gave 56% $(Et_3SiO)_3Sb$, $b_{1.5}$ 160-2°, 1.1037, 1.4681. To 58 g. $[2Pb(OSiEt_3)_2 \cdot Pb(OH)_2]$ in 100 ml. C_6H_6 was added 14.4 g. $TiCl_4$ in C_6H_6 over 1.5 hrs. and the filtered soln. gave 50% $(Et_3SiO)_4Ti$, $b_{2.5}$ 176-8°, m. 96°. The use of $VOCl_3$ similarly gave $(Et_3SiO)_3VO$, $b_{1.5}$ 169-71°, 0.9809, 1.4812. Infrared spectra of the products are reported.

G.M.Kosolapoff.

Organic

Catalytic hydrogenation of diene hydrocarbons with a system of isolated double bonds in the presence of platinum and palladium.

S. A. Kazanskii, I. V. Gostunskaya and A. I. Leonova (M. V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1264-7 (1959).

Hydrogenation of 1,5-hexadiene over Pd black at room temp. in 95% EtOH gave after the uptake of 0.5 mole H_2 27% 1-hexene, 12% hexane and 61% unreacted diene. Similar reaction over Pd black gave 23% 1-hexene, 27% 2-hexene, 33% unreacted diene and 17% 1,4-hexadiene. 2-Methyl-1,5-hexadiene over Pd black gave no 2-methyl-2,4-hexadiene and the reaction mixt. was too complex to be analyzed. 2-Methyl-2,5-hexadiene over Pd gave some 15% 2-methyl-2,4-hexadiene and a mixt. of unidentified products. 2,5-Dimethyl-1,5-hexadiene over Pd black gave some 2,5-dimethyl-1,4-hexadiene and unidentified other products.

G.M.Kosolapoff.

Organic

Ferrocenylboronic and 1,1'-ferrocenylene diboronic acids and their reactions. A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd (M. V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1004-6 (1959).

The reactions were run under N_2. To 92 g. $(BuO)_3B$ in Et_2O there was added with Dry Ice Cooling an ethereal soln. of ferrocenyl-lithium prepd. from 17.6 g. ferrocene by treatment with BuLi (from 39 g. BuCl and 7.6 g. Li); the mixt. was allowed to come to room temp. and on the following day was treated with aq. H_2SO_4, and the org. layer was extd. with aq. KOH; the alkaline exts. on acidification gave first 2.9 g. 1,1'-ferrocenylenediboronic acid (A) (total 13%), dec. 180° (from H_2O), then ferrocenylboranic acid (I), 26%, m. 143-8° (from H_2O). The latter refluxed with aq. $ZnCl_2$ gave ferrocene; the diboronic acid is hydrolyzed similarly. Treatment of I with hot aq. acetone soln. of $HgCl_2$ gave 76% yellow ferrocenylmercuric chloride, dec. 192-4° (from xylene). Similarly aq. $CuCl_2$ gave 84% chloroferrocene, m. 59-60° (from EtOH). $CuBr_2$ gave 80% bromoferrocene, m. 32-3°. A and hot aq. $CuCl_2$ gave 1,1'-dichloroferrocene, m. 75-7° (from EtOH); $CuBr_2$ gave 76% 1,1'-dibromoferrocene, m. 50-1° (from EtOH). Treatment of I with ammoniacal soln. of Ag_2O gave metallic Ag and extn. with Et_2O gave 52% diferrocenyl, dec. 230°, along with 31% ferrocene. Diferrocenyl is sparingly sol. in petr. ether, sol. in MePh, C_6H_6, dioxane and tetrahydrofuran.

G.M.Kosolapoff.

Diferrocenyl.

Organic

O. A. Nesmeyanova and E. G. Perevalova (M. V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1007-8 (1959).

Heating diferrocenylmercury with Pd black gave at best 6.2% diferrocenyl, with ferrocene being the main product (up to 49%). This can be explained by disproportionation of ferrocenyl free radicals formed initially. The products were sepd. chromatographically on Al_2O_3, ferrocene being eluted with petr. ether, diferrocene with petr.ether-C_6H_6. The residues contained some ferrocene polymers. Diferrocenyl is orange, dec. 230°; thermal decompn. does not yield ferrocene.

G.M.Kosolapoff.

Organic

Boron compounds. Reactivity of triallylboron.

A. V. Topchiev, Ya. M. Paushkin, A. A. Prokhorova and M. V. Kurashev. Doklady Akad. Nauk S.S.S.R. 128, 110-12 (1959).

All expts. listed below were run under N_2. Reaction of 60 g. $CH_2:CHCH_2Br$, 48 g. Mg and 37 g. $BF_3.Et_2O$ in 500 ml. Et_2O gave up to 92% $(CH_2:CHCH_2)_3B$, b_{15} 62-5°, d_{20} 0.7178, (I). Addn. of 3.55 g. AcOH to 7.88 g. I gave propylene and 46.9% $(CH_2:CHCH_2)BOAc$, b. 138-40°. I (3.81 g.) and 2.61 g. abs. EtOH gave 52% $CH_2:CHCH_2B(OEt)_2$, b_{10} 43-6°. $CH_2:CHCH_2OH$ and I gave C_3H_6 and $CH_2:CHCH_2B(OCH_2CH:CH_2)_2$, b_6 50-1°. Reaction of 8.8 g. I and 3 g. AcH gave 56.4% $(CH_2:CHCH_2)_2BOEt$, b_7 48-9°. Reaction of 0.6 g. I and 2.1 g. Br_2 in CCl_4 gave undistillable $(Br_2C_3H_5)_3B$, the addn. to the last allyl group requiring some 30 days at room temp. Mixing 1.25 g. pyridine and 2.1 g. I gave an exothermic reaction and a subsequent distn. gave $(C_3H_5)_3B.C_5H_5N$, b_4 116-8°.

G.M.Kosolapoff.

Organic

Intermediate stages of synthesis of tetracyclines.

M. M. Shemyakin, M. N. Kolosov, Yu. A. Arbuzov, Se Yui Yuan, Shen Khuai Yui, K. A. Sklobovskii, M. G. Karapetyan and A. I. Gurevich (N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 128, 113-6 (1959). cf. this j. 112, 869(1957).

Bromination of compds. of type I (R=R'=H; R=H, R'=Ac; R=OMe, R'=H; R=OMe, R'=Ac) in $CHCl_3$ at -60° gave 60-70% corresponding dibromides II (m. 146°, m. 174°, -, -). Oxidation of I with BzO_2H in $CHCl_3$ at 20° gave 85-95% corresponding epoxides III (m. 138°; m. 189°, m. 211°, resp.). Both reactio are stereospecific and yield products with the electrophilic group in the position 3 . The same rule applies to addn. of HOCl or HOBr to I in th reaction of Me_3COCl in aq. Me_2CO at 20° or $(CH_2CO)_2NBr$ in 0.01N aq. Me_2CO soln. of H_2SO_4 at 0°; the 1st of these reactions yields chlorohydrins IV in 75-85% yields (m. 211°; m. 158°; m. 210°, resp.); the 2nd reaction gave the mixed isomeric bromohydrins V and VI in 1:2 ratio, with the addn. takin

place in all cases in positions 2 , 3 . Chlorohydrins or bromohydrins V can be also prepd. by ring opening in III by means of pyridine.HBr or pyridine.HCl in refluxing EtOH. The reverse reaction of ring closure is readily attained with KOH in 70% dioxane. The isomeric halohydrins IV yield the stereoisomeric epoxides VII (m. 141°; m. 191°; m. 174°, resp.). Addn. of HOCl to IX (R=H, or R=MeO) or chlorination in $CHCl_3$ at -50° gave after an aq. treatment with $CaCO_3$ unstable chloroketones X(m. 211°; m. 158°; m. 210°,resp.), while XI (R=H or MeO) similarly gave XII (R=R'=R"=H, X=Cl; R=R"=H, X=Cl; R=R'=H, R=MeO, X=Cl; m. 88°; m. 119°; m.121°, resp.); the analogous bromoketones (m. 64°, m. 57°; m. 70°, and m. 68°, and m. 66°, resp.) are also obtained in 75-90% yields by oxidation of the halohydrins with CrO_3 in 80% AcOH. These halo ketones are dehalogenated with Zn dust in AcOH at 30° to the hydroxy ketones X(R=R'=H, X=H, m.121°; R=OMe, R'=H, X=H, m.192°) or XII (R=R'=R"=H, X=H, m. 135°, and R=R'=H, R"=OMe, X=H, m. 161°), also obtained by hydrolysis of IX with dil. HCl in 70% EtOH at 40°. Reaction of Me_3COK and III(R=R'=H) gave XIII (X=H, Y=OH, X'=Y'=O)(m. 135°) which was oxidized to the corresponding diketo-epoxide, m. 152°. Similarly XIV (Z=O)(m.162°) gave the 3,9-oxide XIII(X=H, Y'=OH, X'=H, Y'=OH; m.176°), through reduction of appropriate I with $LiAlH_4$ to the glycol XIV(m.204°) and its oxidation with BzO_2H. All compds. shown in this paper have the structure of 4a H, 9 OH, 9a H with the cis-conformation of the B and C rings being most stable. Condensation of II with $NaHC(CO_2Et)_2$ in the presence of 2EtONa and hydrolysis gave unsatd.malonate XV (m.127°,). Similar condensation of X(R=R'=H, X=Cl, m.88°) gave 2,9-epoxyketone, m.160°, and theoxomalonate, isolated as bis-p-nitrophenylhydrazone, m.272°. Thus, introduction of functional groups in ring B opens the synthesis of ring A.

Organic

A new method of synthesis of organosilicon aromatic monomers.

E. A. Chernyshev, Li Guan Lian and A. D. Petrov (N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 127, 808-11(1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1958, No.8 no pp given.

Passage of ArX with a Si-H bearing compd. through an empty quartz tube at 550-700° yields arylchlorosilanes. Thus PhCl and Cl_3SiH gave up to 50% $PhSiCl_3$, along with $SiCl_4$ and C_6H_6. The best yield is obtained at nearly 700° with contact time of 15.7 sec. or at 620° with 70 sec. contact. The best ratio of PhCl to $HSiCl_3$ is 2:1. Under such conditions PhCl and $MeSiHCl_2$ gave up to 35% $MePhSiCl_2$, best at 640°. At 640° 1-$C_{10}H_7Cl$ and p-$Cl_2C_6H_4$ gave resp. 60% $C_{10}H_7SiCl_3$ or 50% $C_{10}H_7SiMeCl_2$, or 30% $ClC_6H_4SiCl_3$ and 20% $ClC_6H_4SiMeCl_2$, resp. Any packing in the tube reduces the yields.

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Synthesis of polymers with alternating siloxane and hydrocarbon links.

A. D. Petrov and V. M. Vdovin (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1140-2.

Heating 10.5 g. $Me_2Si(CH_2CH{:}CH_2)_2$, 0.02 ml. 0.1N H_2PtCl_6 in iso-PrOH with 3/4 ml. MeEtSiHCl to 65° resulted in an exothermic reaction, after which the remaining MeEtSiHCl (total 16.3 g.) was added and after 3 hrs. at 180° there was obtained 88% $Me_2Si(CH_2CH_2CH_2SiMe_2^{Et}Cl)_2$ (I), b_3 148-50°, d_{20} 0.9505, n_D^{20} 1.4650. Similarly were prepd.: 92% $O(SiMe_2^{Et}CH_2CH_2SiMe_2^{Et}Cl)_2$ (II), b_2 171.5-2.5°, 0.9616, 1.4597; 84% $(CH_2CH_2CH_2SiMe_2^{Et}Cl)_2$, b_2 109-10°, 0.9651, 1.4610; 82.5% $(CH_2CH_2CH_2SiEt_2Cl)_2$, b_2 132-3°, 0.9705, 1.4666; from appropriate unsatd. silanes. I and H_2O, finally at 40-50° 10 hrs., gave a rubbery polymer with links of $SiMe_2^{Et}CH_2CH_2CH_2SiMe_2CH_2CH_2CH_2SiMeEtO$. II gave an oily polymer with links of $SiMeEtCH_2CH_2SiMeEtO$. The other chlorides gave hard, rubbery polymers on being hydrolyzed with H_2O as above.

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Organic

Alkoxysilanes. XIII. Reaction of siloxanes with alkoxysilanes. New method of synthesis of alkoxysilanes and siloxanes.

M. G. Voronkov (Silicate Chem. Inst., Leningrad). Zhur. Obshchei Khim. 29, 907-15 (1959). cf. 28,2128(1958).

The following starting materials were used to study exchange reactions of alkoxysilanes and siloxanes: $(MeO)_4Si$, m. 4.5°, b_{760} 121°, d_{20} 1.035, n_D^{20} 1.3689; $(EtO)_4Si$, b_{760} 168.3°, 0.93343, 1.3830; $(PrO)_4Si$, b_{10} 107°, 0.9112, 1.4012; $(iso\text{-}PrO)_4Si$, b_{760} 185.5°, 0.8751, 1.3851; $(BuO)_4Si$, b_{10} 150°, 0.89-82, 1.4134; $(iso\text{-}BuO)_4Si$, b_{10} 127°, 0.8857, 1.4068; $[(MeO)_3Si]_2O$, b_1 58°, 1.1222, 1.3806; $(MeO)_8Si_3O_2$, b_1 107°, 1.1355, 1.3869; $[(EtO)_3Si]_2O$, b_1 99°, 0.9979, 1.3915; $(EtO)_8Si_3O_2$, b_1 132°, 1.0300, 1.3950; $(EtO)_{10}Si_4O_3$, b_5 171°, -, 1.3978; $[(EtO)_2SiO]_4$, m. 8°, b_3 156°, 1.0972, 1.4016; $(Me_2SiO)_3$, b_{760} 134.6°, m. 64.5°; $(Me_2SiO)_4$, m. 17.6°, b_{760} 175.8°, 0.9561, 1.3968; $(Me_2SiO)_5$, b_{20} 101°, 0.9597, 1.3982; $(Me_2SiO)_{2760}$, mol.wt. 204700; $(Et_2SiO)_3$, m. 14°, b_{10} 122.5°, 0.9555, 1.4308; $(Et_2SiO)_4$, b_{10} 160°, 0.9636, 1.4358; $(Me_3Si)_2O$, b_{760} 100.4°, 0.7636, 1.3774; $(Et_3Si)_2O$, b_{10} 103°, 0.8443, 1.4340; $(Me_3SiO)_4Si$, $b_{1.5}$ 69°, 0.8675, 1.3892; $(Me_3SiO)_3SiMe$, b_{760} 190°, 0.8500, 1.3879; $(Me_3SiO)_2SiMe_2$, b_{760} 152.5°, 0.8200, 1.3849; $(BuOSiMe_2)_2O$, b_{10} 100°, -, 1.405; Me_3SiOAm, b_{760} 145°, -, 1.4000; $MeSi(OBu)_3$, b_{10} 114°, 0.8771, 1.4109. Distn. of 29.7 g. methylsiloxane polymer (linear or cyclic) with 83.3 g. $Si(OEt)_4$ in the presence of 0.5-1.0 g. KOH gave $Me_2Si(OEt)_2$ in 80-6% yield and a solid residue of substantially SiO_2. Similarly, liq. poly-(dimethylsiloxanes) and $(iso\text{-}BuO)_4Si$ gave 93% $Me_2Si(OBu\text{-}iso)_2$. This reaction with $(Me_3SiO)_4Si$ and $Si(OEt)_4$ gave 78% Me_3SiOEt. Numerous other examples are given for such radical exchange in the presence of KOH. This reaction of 37.1 g. $(Me_2SiO)_4$ with 208.3 g. $(EtO)_4Si$ gave 100% $Me_2Si(OEt)_2$; the filtered residue was heated with a little metaphosphoric acid in a dist app., yielding 42 g. $(EtO)_4Si$ and a residue of poly-(ethoxysiloxanes), b_7 110-280°, from which hexaethoxy and octaethoxy members were isolated. The following products are reported as a result of the above-described disproportionation reactions: Me_3SiOMe, b_{760} 57.2°, -, 1.3679; Me_3SiOEt, b_{760} 75.3

0.7573, 1.3742; Me_3SiOPr, b_{760} 98.5°, 0.7668, 1.3838; $Me_2Si(OMe)_2$, b_{760} 82.2°, -, 1.3705; $Me_2Si(OEt)_2$, b_{760} 113.8°, 0.8401, 1.3814; $Me_2Si(OPr)_2$, b_{760} 152°, 0.8417, 1.3954; $(iso\text{-}PrO)_2SiMe_2$, b_{760} 133°, -, 1.3865; $Me_2Si(OBu)_2$, b_{760} 190.3°, 0.8431, 1.4058; $(iso\text{-}BuO)_2SiMe_2$, b_{760} 172°, 0.8523, 1.3999; $Me_2Si(OAm)_2$, b_{760} 225.5°, 0.8444, 1.4138; $(iso\text{-}BuO)_2SiEt_2$, b_{760} 210°, 0.8455, 1.4130; $MeSi(OMe)_3$, b_{760} 103.5°, -, 1.3701; $MeSi(OEt)_3$, b_{760} 143.5°, 0.8949, 1.3832; $(MeO)_4Si$; $(EtO)_4Si$; $(EtO)_8Si_3O_2$; $(EtO)_6Si_2O$; $[(BuO)_2SiMe]_2O$; $[(BuO)_2SiMeO]_2Si(OBu)Me$, $b_{0.5}$ 165-70°, -, 1.4155; $(Me_3Si)_2O$. The probable scheme of the disproportionation reactions involves equilibria between the consituents of the reaction mixt. and the base catalyst ions.

Cf.Malatesta, Gaz.Ch.Ital.78,747(1948). G.M.Kosolapoff.

Organic

Preparation of ketones containing a tin atom in α-position relative to the carbonyl group.

A.N.Nesmeyanov, I.F.Lutsenko and S.V.Ponomarev (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, 1073-75 (1959). Cf. 120, 1049(1958). Mixing equimolar amounts of R_3SnOMe and an enol acetate results in an exothermic reaction which yields an alkyl acetate and an Sn-bearing ketone, the structure of the latter being confirmed by Raman and infrared spectra. Thus 11.8 g. Et_3SnOMe and 5 g. $AcOMe:CH_2$ gave after 0.5 hr. at 50° some MeOAc and 95% Et_3SnCH_2Ac, b_6 100.5-101°, n_D^{20} 1.4991, d_{20} 1.2875, which with H_2O rapidly gave triethyltin oxide, m. 44°. Similarly were prepd.: 72% 2-oxocyclohexyl-triethyltin, b_4 116-17°, 1.5057, 1.2872; 78% Pr_3Sn-CH_2Ac, b_1 93-100°, 1.4865, 1.1983; 85% Bu_3SnCH_2Ac, b_2 130-32°, 1.4842, 1.1255; and 70% 2-oxocyclohexyl-tributyltin, b_1 155-56°, 1.4805, 1.1290. Attempts to prepare metallate AcM from $AcOCH:CH_2$ and R_3SnOMe failed as the expected product decomposes on distn. It is pointed out that the well characterized Bu_3SnCH_2AC prepared in this work is different from the product of this alleged structure cited by Lesbre et al (Bull. Soc Chim. France, No.10, 1204 (1957)).

G.M.Kosolapoff.

Organic

The character of cyclization of pseudoionone. A new method of preparation of α-ionone.

V.A.Smit, A.V.Semenovskii, V.M.Medvedeva and V.F.Kucherov (N.D.Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk SSSR, 124, 1080-82 (1959). The cyclization of pseudoionone under the influence of 100% H_2SO_4 was studied over the temp. range 60° to -60°. To 15 ml. H_2SO_4 was added 10 g. pseudoionone dissolved in 20 ml. $MeNO_2$ with stirring and the mixture was stirred 3-300 min. after which it was quenched in ice-water and petr. ether. The product, after being washed, was fractionated. The isomeric forms of ionone were estd. by their ultraviolet absorption spectra. At -60° the product is almost devoid of β-ionone even for long runs; at -40° either isomer can predominate depending on the duration of the reaction (prolonged run gives 89% β-form, short run - 72% α-form) and at this temp even 95% H_2SO_4 may be used. At higher temp. the formation of -ionone rises rapidly at at 10° almost no α-ionone is formed regardless of the contact time. Decreased amount of H_2SO_4 (equimolar) tends to increase the content of the α-isomer in the product, but increased amount of H_2SO_4 beyond 6:1 molar ratio does not produce any significant changes. Evidently α-ionone is the primary cyclization product and this isomerizes to β-form especially rapidly at elevated temp. (almost no reaction occurs at -60°). The isomerization is repressed when only 1 mole H_2SO_4 is used for mole of reactant. H_3PO_4 or 60% H_2SO_4 are incapable of inducing the isomerization.

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Organic

Polarography of copper α-alaninate.

E.A.Maksimyuk and G.S.Ginsburg (1st I.P.Pavlov Med. Inst., Leningrad). Doklady Akad. Nauk SSSR, 124, 1069-70 (1959).

Polarographic behavior on dropping Hg electrode was studied for both forms of Cu alaninate (cf. Goldbraikh, Zhur. Neorg. Khim. 1, 1739 (1956)). The study made in 0.1N K_2SO_4 background electrolyte with gelatin maximum suppressor and marcurous sulfate anode, the half-wave potentials of the needle and the plate forms of the salt were found to be different; the needle form has more pos. reduction potential, the actual values being dependent on the concn. of the salt. The results are shown graphically. It is suggested that the needle form may be the cis isomer. The halfwave potentials of Cu glycine salt are more negative than those of the Cu alaninate and with the two substances having similar instability constants this indicates that the glycine salt has the lower specific adsorption. Both forms of Cu salt of glycine and the plate form of the alanine salt show a shift of the halfwave potential to the more pos. direction at relatively high concn. at 50°; at low concns. the halfwave potentials at 20° coincide with those at 50°. The needle form of Cu alaninate shows such a coincidence over the entire extent of the potential-concn. curve.

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Organic

Effect of composition and the conditions of thermal treatment on the structure and the catalytic activity of Al_2O_3-ZrO_2 catalysts.

A.M.Rubinshtein, V.A.Afanas'ev, V.M.Akimov, N.A.Pribytkova and K.I.Slovetskaya (N.D.Zelinskii Org. Chem. Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 1076-79 (1959). Cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 814.

The kinetic data on the behavior of Al_2O_3-ZrO_2 catalysts in decompn. of iso-PrOH are shown graphically in relation to the mode of treatment and the compn. of the catalysts. These catalysts were active at 230°, while pure ZrO_2 begins to function only at 300°. About 15 mole % ZrO_2 is the optimum compn. of the catalyst. The catalyst components, even after heating

to 400-750° show in their X-ray diffraction patterns the distinct features of individual γ-Al_2O_3 and ZrO_2; no solid solns. are formed. The best catalyst activity is found for specimens heat treated at about 600°.

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Organic

Oxidation of n-butane in acetic acid solution by air under pressure. M.S.Furman, A.D.Shestakova, I.L.Arest-Yakubovich and N.A.Lyubitsina. Doklady Akad.Nauk SSSR, 124, 1083-84 (1959).

Kinetic curves are shown for the air oxidation of butane under 60 atm. at 150-165°, with yield curves being shown for EtOAc, MeCOEt and AcOH. The latter was used as an inert solvent for the reaction which was run in steel autoclave with a Ti liner. Co stearate catalyst was used at 0.01% concn. relative to the solvent weight. The duration of runs was 6 hrs. and various rates of air flow were employed to give the kinetic data. Temps. above critical were found to be most desirable as they gave the highest yields of AcOH and the use of the catalyst is desirable for the same reason. All numerical data are in graphical form.

G.M.Kosolapoff.

Organic

Synthesis of organomercury compounds from hydrazones. 2. Reaction of hydrazones of aldehydes and ketones of the alicyclic and the aromatic series with mercuric acetate.

A.N.Nesmeyanov, O.A.Reutov, A.S.Loseva and M.Ya.Khorlina (M.V.Lomonosov State Univ., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 50-61. Cf. this j. 1958, 1315.

To 28.5 g. $Hg(OAc)_2$ and 1 g. $Cu(OAc)_2$ in 250 ml. H_2O at 90° there was added dropwise 5 g. cyclohexanone hydrazone; the exothermic reaction produced N_2 and $Hg_2(OAc)_2$ and finally Hg. The filtered soln. was cooled yielding 1 g. 1-acetomercuri-1-cyclohexene, m. 116-16.5° (from MeOH). The filtrate treated with KCl gave 5 g. 1-chloromercuri-1-cyclohexene, (I), m. 191-92° (from MePh). Similarly, KBr gave 1-bromomercuri-1-cyclohexene, m. 174-75° (from MePh), while KI similarly gave 1-iodomercuri-1-cyclohexene, m. 177-78° (from MePh). I (5 g.) in 10 ml. EtOH was treated with 8.2 g. NaOH in 65 ml. H_2O, mixed with 3.3 g. $SnCl_2$ in 45 ml. H_2O; Hg pptd. immediately and an unpleasant odor developed; after being shaken 1 hr. in the cold, the mixture was extd. with Et_2O yielding 86% bis-1-cyclohexenylmercury, b_{10} 170° (some decompn.); with dil. HCl it gave I. Heating I with concd. HCl on steam bath gave HCl and cyclohexene. If the reaction mixture of cyclohexene and $Hg(OAc)_2$ is kept 2 days in H_2O, then filtered and treated with KCl, there is formed 90% 1-chloromercuricyclohexanol, m. 151-52°. To 42.6 g. $Hg(OAc)_2$ suspended in 200 ml. C_6H_6 there was added at 70° dropwise 5 g. cyclohexanone hydrazone in 50 ml. C_6H_6 and the mixture was filtered after 10 min., and evapd. at room temp. yielding a red oil of 1-acetoxy-1-acetoxymercuricyclohexane, (II) which decomposed on standing and evolved Hg; alkali decomposed it rapidly to Hg and cyclohexanone; alc. $CaCl_2$ gave 1-acetoxy-1-chloromercuricyclohexane, m. 101-105° (from Et_2O). II with cold, alc. KOH gave Hg and cyclohexanone, isolated as the dinitrophenylhydrazone. Reaction of 25.3 g. $Hg(OAc)_2$ and 5 g. 4-methylcyclohexanone hydrazone in H_2O in the presence of 1 g. $Cu(OAc)_2$ gave after the above-described treatment, using aq. KCl, 1.6 g. 4-methyl-

1-chloromercuricyclohexene, m. 171-71.5° (from MeOH). If $Cu(OAc)_2$ is omitted and the reaction is run in MeOH, the final treatment with KCl gave 4-methyl-1-methoxy-1,2-bis(chloromercuri)-cyclohexane, dec. 130-40° (from $CHCl_3$-MeOH), which is decomposed by KOH to Hg and by HCl to HgCl and 4-methylcyclohexanone. From 37.9 g. $Hg(OAc)_2$, 250 ml. C_6H_6 and 5 g. above hydrazone there was formed after filtration and evapn. 9.3 g. oily 4-methyl-1-acetoxy-1-acetoxymercuricyclohexane, which yields $Hg_2(OAc)_2$ with standing, while alc. KOH decomposes it to Hg and 4-methylcyclohexanone; treated with 10% KCl it gave 4-methyl-1-acetoxy-1-chloromercuricyclohexane, m. 159-60°. This with alc. KOH gave the original ketone in the cold. To 50 g. 85% N_2H_4 hydrate and a little BaO there was added 50 g. cyclopentanone, stirred 2 hrs. and extd. with Et_2O yielding 87% cyclopentanone hydrazone, b_5 60-61°, b_{21} 90-91°, d_{20} 1.0030, n_D^{20} 1.5083. This (5 g.) was added at 60° to 32 g. $Hg(OAc)_2$ in H_2O, as above, and after removal of the resulting Hg, the cooled filtrate was treated with KCl yielding 3 g. 1,1'-bis-chloromercuridicyclopentyl ether, dec. above 120° (from aq. Me_2CO), which decomposes rapidly in light and moisture. With alc. KOH this gave Hg and cyclopentanone, isolated as the dinitrophenylhydrazone. If the above prepn. is run in MeOH, the product is 1-methoxy-1-chloromercuricyclopentane, a colorless solid, which decomposes in air and light. Reaction of camphor hydrazone with $Hg(OAc)_2$ as above in C_6H_6 gave an oily 1,1'-di(acetoxymercuri)dibornyl ether, which is decomposed by alc. KOH or HCl; the oil decomposes at 100° yielding Hg; treated with alc. $CaCl_2$ it gave 1,1'-di(chloromercuri)dibornyl ether (XII), m. 153-55° (from Et_2O), which with concd. KOH gave camphor, while heating with concd. HCl gave bornyl chloride. XII was also formed in 98% yield from $Hg(OAc)_2$ and camphor hydrazone in CCl_4, after treatment with $CaCl_2$ as above. Use of excess $Hg(OAc)_2$ in the reaction with camphor hydrazone in H_2O, and treatment with 10% KCl, gave 1,1',3,3'-tetrakis-(chloromercuri)dibornyl ether, dec. 210° (from aq. Me_2CO).